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Vladimir N. Kholodov

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of Sedimentary Rock Formation and Ore Genesis



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Lithology and Mineral Resources (Litologiya i Poleznye Iskopaemye) reviews a wide range of problems related to the formation of sedimentary rocks and ores. Special attention is devoted to comparison of ancient sedimentary rock and ore formation with present-day processes, as the idea of actualism has always constituted one of the bases of the scientific philosophy of lithologists. A major part of the journal is devoted to comparative analysis of sedimentary processes on continents and in oceans, as well as the genetic aspects of the formation of sedimentary and hydrothermal-sedimentary mineral resources. The journal was founded in 1963 by Academician N. M. Strakhov. It will be of interest to lithologists, petrographers, geochemists, mineralogists, ore geologists and metallogenists, as well as to other geologists, ecologists, researchers of experimental and analytical laboratories, and graduate students.

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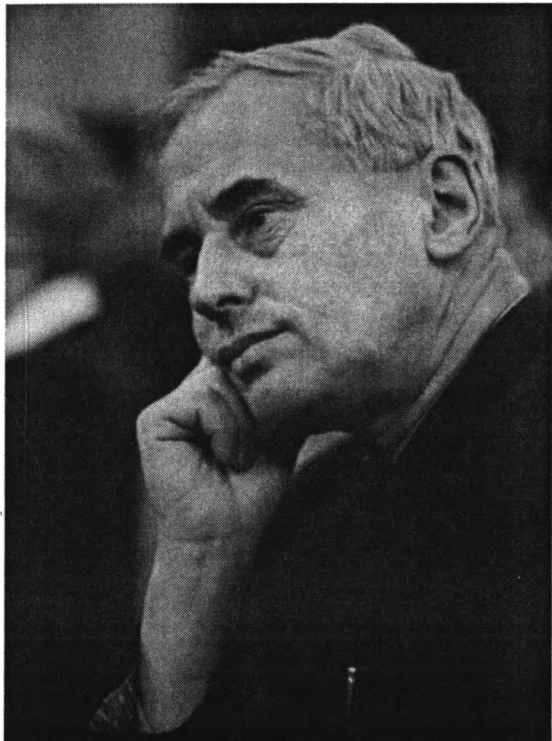
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The 100th Birthday of Roman Fedorovich Gekker

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Roman Fedorovich Gekker, a prominent Russian geologist, lithologist, stratigrapher, and paleontologist was born on March 25, 1900 in St. Petersburg in the family of a doctor of medicine. He studied at the St. Peter Prime German College, which he finished with a gold medal in 1917.

Revolutionary events, which broke the scientific life of the capital, did not halt the activity of a curious youth who prepared himself for research work. In 1917, he entered the Geological Prospecting Faculty of the Mining Institute where he studied until 1923. Simultaneously, in 1920, he became a student of the Geographical Institute and graduated from it in 1925 as a biogeographer.

As studies at the Mining Institute in 1917–1919 proceeded without strict curricula, Gekker could combine lecture attendance with work and started geological research under the supervision of N.F. Pogrebov who became his first teacher in the field of geology and mineral deposits.

Under the supervision of Pogrebov, Gekker was engaged in the compilation of the map of construction materials (1918), the study of sapropel near Ostashkov (1919), and the supervision of pioneer exploration boreholes drilled for combustible shale (kuckersite) and the description of cores (1922–1923).

While studying at the Mining Institute, Gekker attracted the attention of leading representatives of the old mining school of Russia, such as Prof. N.N. Yakovlev, Head of the Department of Paleontology; Prof. A.A. Borisyak, Head of the Department of Historical Geology, later Academician of the Academy of Sciences of USSR; and Prof. D.V. Nalivkin who later was also elected to the Academy of Sciences. These outstanding scientists and lecturers became his first teachers.

Being a student, Gekker assisted Prof. Nalivkin in the Course on *Paleontology* and Prof. Borisyak in the courses on *Historical Geology* and *Geology of Russia*. D.V. Nalivkin, author of the *Study of Facies*, focused much attention on the description of conditions of sedimentation, and the biological aspect of the problem was less elucidated. This circumstance played a large role in the scientific life of Gekker. He was charged with elaborating the paleoecological part of the study.

When preparing the lecture course for students, he heavily used lithological and paleontological data from publications of V.O. Kovalevskii, L. Dollo, O. Abel, K.F. Rul'e, N.I. Andrusov, A.D. Arkhangel'skii, A.P. Karpinskii, and M.E. Noiniskii, as well as materials of Russian zoologists on the Black Sea, Barents Sea, and White Sea (S.A. Zernov, K.M. Deryugin, E.F. Gur'yanova, I.G. Zaks, and P.V. Ushakov). However, he leaned upon his own geological experience obtained during researches in 1929–1931 to highlight several specific geological problems. His work had an applied significance. It was devoted to a comprehensive study of the Main Devonian Field, including the description of stratigraphy, the compilation of geological map, and the characterization of mineral deposits.

The Main Devonian Field served for Gekker as a natural textbook on marine paleoecology. The material collected from this field was so huge that it could be used for the compilation of a large section in the Course of *Paleoecology*, as well as for the elaboration of the *Manual on Paleoecology*. This small book (40 pages and 10 plates), published in 1933, was the first method-

ical manual on paleoecology in the world. It formulated principal objectives of paleoecology and substantiated the necessity for joint efforts of lithologists and paleontologists for reconstructing the habitat of ancient organisms, sedimentation environments, and genesis of mineral deposits. Basic conclusions of the manual were translated into German and, therefore, became readily available for foreign scientists.

Gekker delivered the Course on *Paleoecology* for the first time at the Petrograd Mining Institute in 1932. Simultaneously, he delivered it at the Leningrad University until 1935. Since 1941, he delivered the course at Moscow University for almost 20 years. It became a peculiar crystallization center of his whole activity. On the one hand, research works of Gekker were reflected in the form of upgraded examples showing the complexity of paleontological problems. On the other hand, the course on *Paleoecology* gave an impetus to the publication of splendid works, such *Directions for Research on Paleoecology* (1954) and *Introduction to Paleoecology* (1957), the latter being the first manual in the world literature on the subject. Both books were translated in France (1955, 1960), China (1956, 1957), Japan (1959), Poland (1963), and the United States (1965).

The line of investigation presented in the books was highly appraised by the scientific community. In 1935, Gekker got his PhD degree in Biology without the official defence procedure and in 1937, he defended the DSc dissertation *Paleoecological Method of Research in the Practice of Geological and Biological Sciences*.

Gekker substantiated two principal directions of his activity in these works. He called paleontologists for a deeper investigation of the relationships between old organisms and facies environment and the application of lithological and paleontological reconstructions for revealing regularities in the distribution and formation conditions of sedimentary mineral deposits.

In the late 1920s, Gekker was invited by Borisyak to the Geological Museum of the Russian Academy of Sciences to fill the position of a researcher. In 1930, he joined the newly founded Paleozoological (later Paleontological) Institute. Since that time, the scientific activity of Gekker was entirely associated with the Paleontological Institute (PIN) of the Academy of Sciences of the USSR where he worked for 67 years and celebrated 90th birthday in 1990.

During the work at the Paleontological Institute, Gekker and his collaborators studied Devonian, Carboniferous, and Permian rocks of the Russian Platform, Urals region, and Kuznetsk Basin, Jurassic rocks of the Volga region and Kazakhstan, Neogene rocks of the Caucasus, and Paleogene rocks of the Fergana Valley. The studies completely elucidated the life of marine paleobasins and helped a better understanding of regularities in sedimentation and distribution of sedimentary mineral deposits therein.

The wide experience gained by Gekker by the early 1950s allowed him (the only one among paleontologists) to participate in the discussion on sedimentary rocks, present some results of application of the method of complex paleoecological study of sediments, and substantiate the necessity of comparative lithologic study of paleobasins for the whole time of their existence (Gekker and Osipova, 1951).

The series of works of Gekker and his colleagues (D.V. Obruchev, V.P. Barkhatova, N.N. Forsh, M.F. Filippova, and others) is of special interest for lithologists. It is devoted to the Devonian paleogeography of the Russian Platform. The works were published during the period from 1930 to 1934.

Based on works of P.N. Venyukov, F.M. Zhenzhurist, V.A. Shchirovskii, S.V. Obruchev, A.D. Arkhangel'skii, V.N. Krestovnikov, F.N. Chernyshev, and others, as well as his own descriptions of geological sequences, the study of fauna samples, and the geological mapping of the Main and Central Devonian fields of the Russian Platform, Gekker elaborated the stratigraphic scheme of studied sedimentary sequences and correlated them in a unified profile. He distinguished three stages in the Devonian history of the platform. He revealed that land predominated in the Early and Middle Devonian, whereas sea prevailed in the Late Devonian. The sedimentation proceeded under conditions of a hot and arid climate, the Fennoscandian Shield being a steady provenance elevated above the surface.

Devonian shallow marine sediments can be clearly divided into the following facies: (1) coastal sandy- and clayey-calcareous sediments with abundant fucoids; (2) facies of dominating brachiopod coquina; (3) coquina-conglomerate facies having perforated pebbles covered with shells and tubes of attached organisms; (4) facies of a solid flattened calcareous bottom with a similar population; (5) facies of a solid bottom with large burrows descending from the bed surface; and (6) stromatopore-algal banks.

Benthonic organisms occur on the floor of the Devonian paleobasin in compliance with the distribution of sediments. Gekker wrote that lingulids kept close to the coast or calm water and were buried into sand, calcareous clay, or calcareous ooze; brachiopods attached with the help of a pedicle (*Spiriferidae*, *Atrypidae*, *Athyridae*, and *Rhynchonellidae*) lived in colonies and preferred astatic waters; along with shell-attached pelecypods (*Limanomia*) and crinoids, brachiopods attached with the help of a shell (*Isboskites*) covered pebbles and hard bottom; auloporids and worms (*Spirorbis* and *Serpula*), which lived under similar conditions, often occupied shells of brachiopods then alive; blue-green algae (*Girvanella* and *Pycnostroma*) and stromatopores avoided the coastal area of sea and lived far away from it; the same is true of tetracorals (*Cyathophyllum*) and others to a greater extent (Gekker, 1934, p. 367).

Sedimentary deposits of clays, bauxite-like rocks, glass and foundry sands, limestone, dolomite, and gyp-

sum were a major preoccupation of Gekker in works devoted to the Devonian cycle. He showed that clays and bauxite-bearing rocks were closely related to the redeposition of weathering products developed on Devonian crystalline rocks and that quartz sands more often occurred in areas where Middle Devonian continental red sandstone was reworked by seawater and the ferruginous jacket over quartz grains was removed. Besides, Gekker established that limestones of the Pskov, Chudovo, Shelon, and Elets sequences represent the deepest facies of the Devonian paleobasin and are closely related to sea transgressions. In contrast to them, dolomite and gypsum-bearing sediments probably accumulated in salty lagoons that were partly separated from the Devonian sea. This inference is well confirmed by poor benthonic fauna. It also makes it possible to relate the above-mentioned mineral deposits to sea regressions.

The series of works devoted to the lithology, facies, paleoecology, paleogeography, and mineral deposits of Devonian rocks in central Russia culminated in the first exhibition "Life in the Devonian Sea" organized by Gekker in the Museum of the Paleontological Institute, Academy of Sciences of the USSR.

The study of Jurassic clays and carbonate shales of the Karatau region, Kazakhstan, carried out by Gekker in 1936, is of great importance for solving some lithologic problems. The work culminated in the publication of a collection of articles *The Jurassic Fossil Lake in the Karatau Range* (Moscow-Leningrad, Akad. Nauk SSSR, 1948, p. 109). The collection also included works by M.F. Filippova, a lithologist, E.S. Rammel'meyer who described mollusks, as well as A.N. Ryabinin who studied fossil remains of flying pangolins and turtles.

Jurassic rocks occur within the Leont'ev Graben located between the Greater and Lesser Karatau and bounded by two NW-striking faults. The Jurassic Section, which is characterized by a complicated structure and great thickness, can be divided into four horizons. The Lower Jurassic horizon is represented by sandy-conglomerate and coal-bearing sequences about 500 m thick. The coal-bearing sequence comprises various flora of fern, ginkgo plants, bennettitales, as well as swamp-type coniferous plants. The overlying Middle Jurassic horizon is composed of tabular sandstone and conchoidal shale (thickness 500–650 m). The Upper Jurassic horizon is represented by alternating conglomerate, sandstone, fine-laminated calcareous shale, and thin-bedded dolomite with abundant fauna and flora. The horizon contains numerous plant, fish and insect fossil remains. The thickness is 70–100 m. The section is crowned by a horizon of massive, more rarely foliated, limestone and dolomite, up to 50 m thick, which are arbitrarily assigned to the Jurassic.

The genesis of Jurassic rocks in the Karatau Range has long been the subject of much controversy. V.G. Mukhin and A.I. Turutanova-Ketova supposed that the sequence formed in a large sea basin. V.N. Ve-

ber argued that it was of the continental origin. Z.F. Gorizdro-Kul'chitskaya and D.V. Nalivkin were inclined to believe that it was of fresh-water or even lacustrine-swamp genesis.

The paleoecological analysis by Gekker allowed to carry out a reconstruction of the Jurassic sedimentation. He suggested that abundant, well-preserved remains of ganoid fish, which could be transient, and a single specimen of a water turtle give nothing for the characteristics of the chemical regime in the Karatau Basin. However, rare remains of estheriids indicate that the basin was fresh-water rather than saline (marine). Smaller scanty gastropods and, especially, the absence of pelecypods also indicate the lack of any connection between the Karatau Basin and sea. These data, and the current ecological features of these groups suggest unfavorable conditions for the life of mollusks, i.e. highly carbonate water. Such a conclusion agrees well with the petrographical composition of fine-laminated calcareous shales, which represent a thin alternation of dolomite and limestone laminae (Gekker, 1948, p. 117).

Furthermore, analyzing the distribution of Jurassic insects in the Karatau Basin, Gekker emphasized that orders with the water larval stage of evolution were absent. This fact confirms the inference that we deal in this case with a lake basin hydrochemically resembling the present-day Lake Balkhash. As is shown in works by Strakhov (1945) and Sapozhnikov (1942), the thin calcareous-dolomitic mud closely associates with clayey material in deep parts of Lake Balkhash and is chemically formed owing to a high alkali metal reserve, high pH values of lake waters, and intense diagenetic processes in muds. Thus, the comparative lithologic method fully confirms paleoecological data.

The chart compiled by Gekker is of great methodical interest for lithologists. It substantiates inferences on the type of the Karatau Basin the salinity and hydrodynamics of its waters and the type of bottom sediments and topography of the surrounding land. Jurassic fossils, which are collected in recent years, do not refute earlier assumptions on specific features of the Jurassic lake.

The study of fish remains was subsequently continued in Maikop sediments of the Greater Caucasus where Gekker and Merklin (1946) registered a high rate of dead fish burial, scarcity of benthonic associations, and possible hydrogen sulfide contamination of bottom water. This small article of Gekker and Merklin was later used by several researchers (R.L. Merklin, A.S. Stolyarov, M.M. Mstislavskii, A.V. Kochenov, and others) for interpreting the genesis of U-bearing fish cemeteries in the Mangyshlak Peninsula and some other regions of Kalmykia and the Lower Volga region.

In collaboration with A.I. Osipova and T.N. Bel'skaya Gekker published a major work entitled *The Fergana Bay of the Paleogene Sea in Central Asia: Its History, Sediments, Fauna, Flora, and Their Habitat*, Moscow: Akad. Nauk SSSR, 1962, 2 vols.

The authors started field investigations during the Great Patriotic War in 1943 and continued for four more years with some interruptions. They studied 56 Paleogene sequences at the Fergana piedmont. Based on previous works of stratigraphers (K.P. Kalitskii and O.S. Vyalov) and their own paleontological observations, they correlated the sequences, distinguished different stages and facies complexes of Paleogene rocks, and described typical fauna and flora. For each of eight distinguished stages, they compiled paleogeographic maps (and schemes) and carried out the detailed paleoecological analysis.

The correlation of the maps and schemes showed that periods of the lagoonal, terrigenous, and carbonate sedimentation can be distinguished in the Paleogene history of the Fergana Bay. The bay was located in an arid and hot climate zone. It accumulated flows from several rivers and was connected with an open sea through two passages. Changes in the normal hydrogeologic regime resulted in the salinization or desalting of water that immediately affected the fauna and flora.

Red sediments, which are widespread in lower stages of the Paleogene, attracted the particular attention of researchers who established that the sediments represent typical deltaic complexes. The researches also revealed that intense dolomitization occurred in the Fergana Bay both in saline lagoons and in the whole bay area during the periods of its separation and desalting. Such dolomitization represents a specific type of the process that was previously unknown in the geological literature.

Gekker and his coauthors revealed that the Fergana Bay was populated by foraminifers, radiolarians, boring sponges, worms (tubicolous, fossorial, and boring), bryozoans, bivalves, gastropods, echinoderms (sea urchins and ophiuroids), arthropods (ostracodes, barnacles, medium-tailed crayfish, and crabs), fishes (sharks, batoids, and teleosts), as well as various groups of algae. Oysters and other bivalves, gastropods, ostracodes, medium-tailed fossorial crayfish, crabs, and smaller benthonic foraminifers dominated. Representatives of other group were rare. Typical inhabitants of holosaline seas (echinoderms, corals, are planktonic foraminifers) were very rare. Nummulites, brachiopods, and cephalopods typical of coeval basins in southern Europe and North America were absent.

The quantitative paleoecological study of all fossils allowed the researchers to distinguish bottom assemblages of the Paleogene fauna and outline its distribution in different facies zones and areas of the bay.

Large oysters, the most abundant group of mollusks in the Paleogene Fergana Basin, were more comprehensively studied with a wide use of actualistic data. The detailed study of all types of oyster types made it possible to establish the composition of oyster biocoenoses, conditions of their life and death, and processes of the occupation of different zones by oysters

and, finally, to distinguish oyster biocoenoses and thanatocoenoses.

The problem of oil-yielding strata, especially urgent for such a large oil-and-gas province as Fergana, was discussed in detail in the work. The authors proved that main oil-yielding strata are represented by components of carbonate sequences rather than clay members between carbonate rocks. This inference agrees well with the most recent data on petroleum geology in western countries.

During the 1960s, in accordance with decisions of the All-Union Conference on the State of Paleontology in the Soviet Union (1954), Gekker was engaged in the study of echinoderms. He published *Manual for Studies on Paleoecology* (1954, 1955) and *Introduction to Paleoecology* (1957). At the same time, he continued studies on the paleoecology of the Kazanian, Carboniferous, and Devonian seas of the Russian Platform. Results of these works are reflected in a series of articles and two monographs.

In 1987, his last book *On the Silurian Plateau* devoted to the history of the geological study of the "cradle" of the Russian paleontology was published.

Gekker gave much effort to the popularization of paleoecological studies in press, reports, and lectures. Guest sessions on paleoecology and lithology, which were organized by Gekker in 1962–1968 in collaboration with scientific and production institutions of different regions of this country, represented a new form of popularization and a peculiar kind of workshops for researchers, applied geologists, and lecturers of educational institutions. Participants of the sessions became acquainted with the most interesting localities of old fauna and methods for their study.

Gekker's scientific-popularization activity was versatile. He organized a team of paleontologists and painters for the compilation of the Atlas *Evolution of Life on the Earth*, participated in creating a documentary film on the same theme and a film strip about A.P. Karpinskii, helped paleontologists, sculptors, and painters who worked on decorating the new building of Moscow State University in the 1950s, etc. His relations with local museum specialists and workers of the All-Union Wildlife Preservation Society were very close and cordial. In 1970, he joined in the fight for the protection of Lake Baikal. In 1974, Gekker founded and headed the Section on the Preservation of Paleontological Monuments of the All-Union Paleontological Society and became its Honorary Chairman since 1984.

All the aforesaid enables us to recognize that Gekker was not only a prominent scientist who developed a new and original line of science but also a leader of the Russian school of paleoecologists. Many young lithologists and paleontologists follow in his footsteps.

Gekker's scientific research was highly appraised. He was elected Honorary Member of the All-Union Paleontological Society and the Moscow Society of Naturalists, Corresponding Member of the German

Paleontological Society and Zenkenberg Society of Naturalists (Germany), Member of the French Geological Society, Honorary Member of the Hungarian and Bulgarian Geological societies, Honorary Doctor of the Lyons University, and Member of the Swedish Geological Society. The efficiency of paleoecological studies of paleobasins was demonstrated by the International Project "Ecostratigraphy." Such works were developed in many countries. In France, the method elaborated by Gekker is known as the synoptic method and is recognized as being of great value for the reconstruction of ecosystems and ecogenesis of groups. The recognition of Gekker's credits in the development of paleoecology was also expressed in the fact that he was elected Chairman of the Paleontological Section of the International Paleontological Union in 1968. In 1983, the First International Paleoecological Congress was held in France to honour R.F. Gekker. The congress attracted more than 300 scientists from 30 countries.

Gekker was awarded with the Order of Lenin, two orders of "Badge of Honour," and six state medals. The Chinese government decorated him with the Medal "Chinese-Soviet Friendship." In the Soviet Union, the Order of Lenin was generally awarded to mark a long-term and irreproachable work. Such was the activity of Roman Fedorovich Gekker in the Academy of Sciences during 67 years and all his life as well. He passed away on August 15, 1991.

The 100th birthday of Gekker was widely commemorated at the session of the Paleontological Society in

St. Petersburg, at the All-Russia Symposium in Novosibirsk, and at the International Conference in Moscow. Many articles and collections of works of Russian scientists are devoted to him.

There is no question that Gekker has performed great services for the Russian science. He left a fond memory in scientific works forever.

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Authigenic Carbonate and Barite Mineralization in Sediments of the Deryugin Basin (Sea of Okhotsk)

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Abstract—Results of the analysis of mineralogy, geochemistry, and isotope parameters ($\delta^{13}\text{C}$, $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$) of carbonates and barites from sediments of the Deryugin Basin in the Sea of Okhotsk are presented. The diagenetic nature of carbonates and barites, which are formed as a result of the prolonged activity of cold seeps acting along a fracture zone and supplying methane- and barium-saturated fluids, is determined. Any signs for hydrothermal activity were not observed.

In recent years, a significant progress was achieved in the study of local manifestations of carbonate and barite mineralization in seafloor areas where the discharge of cold, gas-saturated fluids takes place (venting zones). Such phenomena are described in different geological conditions. Most of them are found within accretionary prisms of subduction zones on active continental margins of the Pacific Ocean (Ritger *et al.*, 1987; Han and Suess, 1989; Kulm and Suess, 1990; Lallemand *et al.*, 1992; Thornburg and Suess, 1992; Dia *et al.*, 1993; Sample *et al.*, 1993; McAdoo *et al.*, 1996; Seliverstov *et al.*, 1994; Bohrmann *et al.*, 1998; Suess *et al.*, 1998), the Indian Ocean (Von Rad *et al.*, 1996), and the Atlantic Ocean (Faugeres *et al.*, 1990). Similar manifestations are also known from marginal seas (Astakhova *et al.*, 1987, 1990, 1993; Zonenshain *et al.*, 1987; Lein *et al.*, 1989; Torokhov *et al.*, 1991; Ginsburg and Solov'ev, 1994; Ginsburg *et al.*, 1993; Taran *et al.*, 1992), passive continental margins of the Atlantic Ocean (Roberts *et al.*, 1990, 1992; Paull *et al.*, 1992; Fu *et al.*, 1994; Ferrel and Aharon, 1994), and intracontinental seas (Ginsburg and Solov'ev, 1994; Jorgensen, 1992). Fluid discharge zones are often accompanied by carbonate and, more rarely, barite mineralization and gas hydrates.

Numerous investigations established that carbonate crusts and concretions are formed in the areas of cold seeps of gas-saturated fluids mostly as a result of the microbial oxidation of methane delivered from deep levels of sedimentary sequences along fracture zones (Kulm and Suess, 1990; Paull *et al.*, 1992; Roberts and Aharon, 1994; Suess *et al.*, 1996, and others). The oxidation of methane by bacteria is accompanied by the local oversaturation of water, which is contained in soft sediments, with carbonate ion and the settling of carbonates in the form of a hard mineral phase. In the case of the enrichment of fluids with Ba, authigenic barite

also precipitates, in addition to carbonates (Commeau *et al.*, 1987; Dia *et al.*, 1993; Fu *et al.*, 1994; Torres *et al.*, 1996a, Suess *et al.*, 1998). To date, the mechanism of this process is not completely revealed. There is a lively discussion on the way of barite formation proposed by Goldberg and Arhenius (1958), according to which biogenic barium is remobilized in a sulfate-depleted zone of sedimentary sequence; as a result of the subsequent migration toward overlying sedimentary layers and the interaction with sulfate ion of interstitial water, the biogenic Ba precipitates in authigenic barite fronts (Dean and Schreiber, 1978; Von Breyman *et al.*, 1992; Torres *et al.*, 1996b). In such a case, the authigenic barite is enriched with the heavy sulfur isotope related to the metabolism of sulfate-reducing bacteria (Mizutani and Rafter, 1973; McCready and Krouse, 1980). It was also established that barites can settle during the mixing of barium-saturated fluid, which ascends from deep sedimentary layers, with sulfate ion near (or on) the water-sediment interface, when fluids directly emanate through the seafloor (Torres *et al.*, 1996b). In such a case, barites inherit the isotopic composition of sulfur from sulfate ion of seawater.

For the first time, barite samples were recovered in the Deryugin Basin by B.I. Vasil'ev on the 15th cruise of the R/V *Kallisto* in 1981 during the dredging of the northern slope of a small submarine high with an absolute depth of 1460 m. Subsequently, they were identified by Astakhova *et al.* (1987) as "travertine-like" barites. The repeated dredging was carried out on that site approximately 3 km eastward (23rd cruise of the R/V *Pegas* in 1986), and barites and carbonate concretions were encountered as well. Results of these investigations were presented in publications by Astakhova *et al.* (1987, 1990). These authors referred the barites to as hydrothermal formations. Subsequently, during the

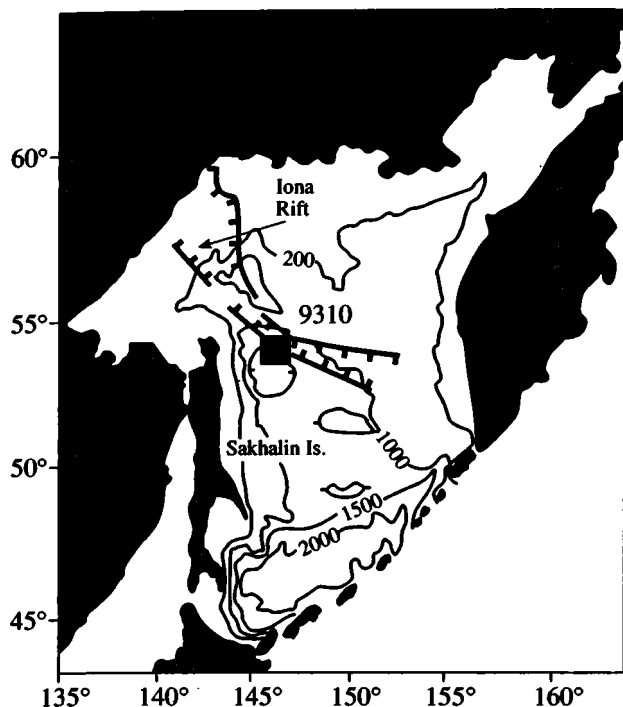


Fig. 1. Schematic location of Station 9310 with carbonate-barite mineralization on the eastern flank of the Iona Rift in the Deryugin Deep.

25th cruise of the R/V *Akademik Nesmeyanov* (1993), one of the authors of the present work executed in this area a sampling with a hydrostatic sampler (Station 9310; waterdepth 1507 m; 54°00'07" N, 146°17'00" E), which recovered a Pleistocene-Holocene sedimentary sequence, 125 cm thick, with numerous carbonate-barite inclusions of variable morphological types (Figs. 1, 2).

TECHNIQUE OF INVESTIGATIONS

Samples of calcite, barite, and host sediments were studied by optical (description of thin sections and grain-size fractions) and scanning electron microscopy (SEM), with the use of energy-dispersive X-ray device (EDAX) for defining the elementary composition of minerals at GEOMAR (Germany). The X-ray structural analysis was carried out at GEOMAR and Pacific Oceanological Institute. In this process, the standard reference curves were used to define the Mg content (mol % Mg) in carbonate formations. The isotopic composition of carbon and oxygen in calcite was analyzed at GEOMAR with the use of a FINNIGAN MAT-252 mass-spectrometer. The isotopic composition of sulfur and oxygen in barite was defined using a FINNIGAN MAT-251 mass-spectrometer, and that of strontium by a FINNIGAN MAT-262 thermal ion-spectrometer at the Geological Institute in Bochum (Germany).

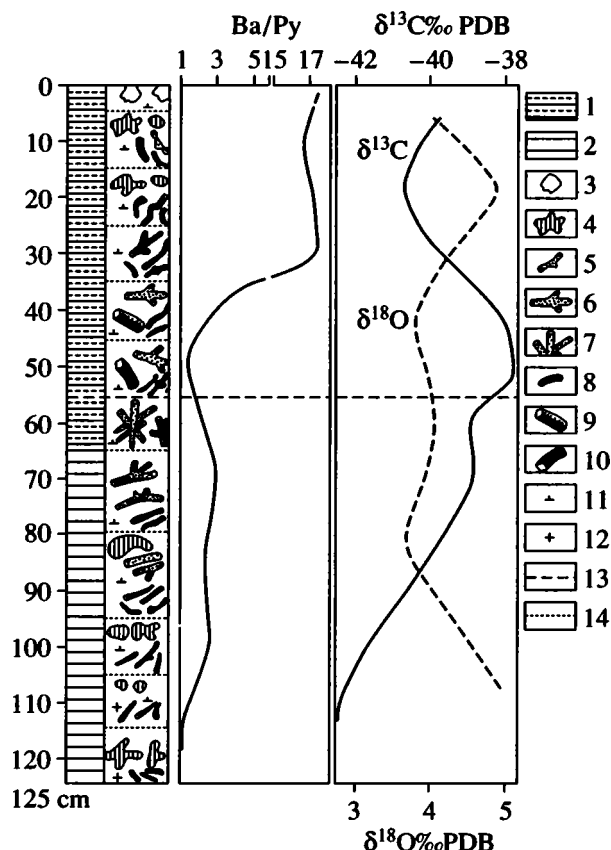


Fig. 2. Distribution of types of carbonate-barite inclusions in sediments from Core 9310. (1) Psammitic silt, (2) pelitic silt, (3) fragments of consolidated silt-clay sediment; morphological types of carbonate-barite inclusions: (4) calcite concretion, (5) individual, tubular calcite and calcite-barite bodies, (6) dendritic, tubular barite-calcite bodies, (7) complex polytubular-dendritic bodies, (8) barite tubes of a small diameter, (9) hollow calcite-barite tubes of a large diameter, (10) the same but filled with barite crystals with different morphologies, (11) individual barite crystals and their aggregates, (12) barite beads (microconcretions); (13) Pleistocene-Holocene boundary, (14) sampling horizons. (Ba/Py) barium to pyrite percentage ratio in 0.05–0.1 mm fraction; $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbon and oxygen isotopes in carbonate inclusions.

GEOLOGICAL SETTING AND SEDIMENT COMPOSITION

The Deryugin Basin is situated in the western part of the Sea of Okhotsk, close to the seashore of Sakhalin Island (Fig. 1). This basin has an oval shape (in plan) and is bounded by the 1550-m contour line. It has a maximal waterdepth of 1750 m and an irregular topography. The western and central parts represent a flat bathyal plain, slightly rising toward the slopes of the basin. In the northeast, the relief is more irregular and complicated by several small submarine mountains and highs with a southwestern strike.

In geostuctural terms, the western part of the basin represents a subsided block of the Earth's crust overlain by a sedimentary cover, more than 2 km thick. Accord-

ing to recent data (Gnibidenko, 1990; *Cruise ...*, 1997), the eastern part of the basin is the young Iona rift system (Fig. 1) characterized by a block structure of the basement with numerous faults, including normal ones. Elevated blocks of the basement look like small rises and separate mountains with a relative elevation of up to 100, more rarely 200 m. Based on seismic profiling data, the highs are covered by sediments and sedimentary rocks (*Cruise ...*, 1999). The manifestation of carbonate-barite mineralization was discovered just on the slope of one of these rises.

Increased values (relative to the surrounding areas of the Sea of Okhotsk) of heat flow, averaging 82.7 mW/m², are recorded in the Deryugin Basin. Maximal values of heat flow are observed on the elevated basement blocks in tectonic disturbance zones. In particular, to the east of Station 9310, the heat flow ranges from 109 to 155 mW/m² in a fault zone representing the northern boundary of the high with manifestations of carbonate-barite mineralization (Hayashi, 1997).

The Sea of Okhotsk is one of the biologically high-productive areas of the World Ocean with a large flux of organic carbon to the seafloor (Koblents-Mishke, 1967; Bogorov, 1974). The belt of sediments with a high content of organic carbon (more than 1.5%) is traced in the form of a wide strip located on the continental rise and in the adjoining basins, including the Deryugin Basin (Bezrukov, 1960; Lisitsyn, 1978). These areas are characterized by high sedimentation rates attaining 150–200 mm/ka (*Sovremennoe ...*, 1997).

Core 9310 is made up of dark gray, terrigenous clayey silt (patchy at the level of 2–25 cm) with an admixture of sand and gravel particles and lumpy structure. Slightly indurated clay lumps with obscure contours, up to 20 mm in size, are encountered among soft sediments. At the top (0–5 cm), we found consolidated clay fragments (15–30 mm in diameter), speckled with numerous fucoids with a diameter of less than 1 mm. These fragments do not differ in composition from the host sediments. In the upper part of the core, sediments are slightly enriched in siliceous detritus (diatoms and radiolarians). Carbonate, barite, and carbonate-barite tubular bodies with variable morphology and size are encountered throughout the entire core (Fig. 2). Any regularity in the distribution of these inclusions in sediments is not revealed. Their total quantity and the ratio of different types significantly vary from horizon to horizon.

Based on micropaleontological determinations (the diatom analysis carried out by I.B. Tsoi), the upper (0–55 cm) interval, which is slightly enriched in diatoms, can be referred to as Horizon 1 distinguished by Zhuze in the Sea of Okhotsk for Holocene sediments (Zhuze, 1962; Bezrukov, 1960; Gorbarenko *et al.*, 1988; Gorbarenko, 1991, and others). The sedimentation rate during the formation of this horizon was around 50–60 mm/ka.

The data of X-ray analysis and microscopy showed that sediments containing carbonate concretions and tubular inclusions are carbonate-free. Some admixture of CaCO₃ in the form of calcite is noted in sediments from the lower (55–65 cm) interval adjoining polytubular barite-calcite inclusions. The maximal number of polytubular inclusions were found in this horizon. On the other hand, the presence of barite in host sediments is practically established throughout the entire core. Barite occurs here in the form of small (0.01–0.1 mm) crystals and their aggregates, along with larger fragments of tubular inclusions. It is well seen when studying smear-slides of sediments and composition of silt- and sand-sized heavy fraction from these sediments (the density is more than 2.89 g/cm³). The barite content in this fraction is 42–63%. In addition to barite, pyrite is also present in the sediments (25–37%). Its quantity sharply increases starting with the 30-cm level (Fig. 2).

MINERALOGY OF CARBONATE-BARITE INCLUSIONS

Based on the microscopic study of thin sections and grain-size fractions of sediments washed out from clay particles, along with the electron microscopy and X-ray analysis data, we can distinguish the following mineralogical types of authigenic carbonate-barite inclusions: (a) tubular calcite, barite-calcite, and barite bodies; (b) calcite concretions with different density values; and (c) barite spherulites, separate barite crystals, and their aggregates. These morphological types of carbonate inclusions are similar in mineral composition. Based on the X-ray structural analysis (Table 1) and microscopy data, they consist of predominantly cryptocrystalline magnesian calcite (10–15 mol % Mg), which cements the terrigenous clayey-clastic matrix and organic detritus (diatoms, radiolarians, sponge spicules, etc.), and infills the intergranular pore space. Barite is present as a minor admixture.

Tubular inclusions. The core contains different morphological types of tubular bodies with calcite, calcite-barite, and barite mineralization. Their size changes within a wide range. Elongated individual tubes, 3–6 mm in diameter and up to several centimeters long, predominate. Branched tubes with several lateral sprouts, or tightly intergrown aggregates of calcite-cemented and differently oriented individual tubular bodies are rare. They are found at levels of 45–55 and 70–95 cm. Complex (dendritic) polytubular build-ups (size up to 60–100 mm) slightly differ from the individual bodies and consist of numerous tubular bodies with a variable diameter (from 2–3 to 15 mm). They are observed at the level of 55–80 cm. Their surface is rugged and cavernous due to an irregular mineralization of the host sediment. Walls of the tubes are fragile, easy breakable, and crushable.

The internal structure of the group of tubular bodies under consideration is also characterized by a large

Table 1. Values of oxygen and carbon isotopes, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and mineralogy of carbonate and carbonate-barite inclusions from sediments of the Deryugin Basin (Sea of Okhotsk)

Station no. and horizon, cm	Type of authigenic inclusions	$\delta^{18}\text{O}$, ‰ PDB	$\delta^{13}\text{C}$, ‰ PDB	$^{87}\text{Sr}/^{86}\text{Sr}$	Mineralogy**
9310 (5–15)	Soft calcite concretion (type Cc ₁)	+4.08	–39.75	0.708651	Mg-calcite (11 mol % Mg), rare barite
9310 (5–15)	The same (type Cc ₁)	+4.40*	–40.30*	–	The same
9310 (5–15)	Calcite tube (type Tc ₁)	+4.08*	–40.24*	–	Mg-calcite, rare barite
9310 (15–25)	Hard calcite concretion with small channels filled with barite (type Cc ₂)	+4.66	–40.57	0.708716	Mg-calcite (11 mol % Mg), rare barite
9310 (15–25)	Fragment of mollusk shell	+3.74	–3.79	–	Calcite
9310 (35–45)	Calcite-barite tube (type Tc ₂)	+3.83*	–38.19*	–	Mg-calcite, barite
9310 (45–55)	The same (type Tc ₂)	+3.97	–37.59	0.708665	Mg-calcite (11 mol % Mg), barite
9310 (55–65)	Polytubular calcite aggregate with rare barite channels (type Tc ₂)	+4.02	–38.91	0.708726	Mg-calcite (12 mol % Mg), barite
9310 (65–80)	Calcite tube with small channel filled with barite (type Tc ₃)	+3.90	–38.73	0.708685	Mg-calcite (13 mol % Mg), barite
9310 (80–85)	Dense calcite concretion with rare barite channels (type Cc ₃)	+3.79	–39.74	0.708636	Mg-calcite (15 mol % Mg), barite
9310 (85–95)	Barite tube with external, thin calcite crust (type Tb ₂)	+4.12	–40.52	0.708722	Mg-calcite (13 mol % Mg), barite
9310 (105–115)	Massive calcite concretion (type Cc ₃)	+4.88	–42.25	0.708692	Mg-calcite (10 mol % Mg), barite
9310 (105–115)	Flattened, massive calcite concretion (type Cc ₃)	+4.89*	–42.86*	–	The same
LV27-2 (570–580)	Soft, authigenic calcite crystals	+3.00	–16.58	–	Calcite (7 mol % Mg)
B37-07	Dense calcite-aragonite crust	+3.64	–48.85	0.709099	Aragonite, Mg-calcite
B37-07	Fragment of mollusk shell	+2.97	–2.73	0.709149	Calcite

Note: Location of sampling stations: (9310) Deryugin Basin (waterdepth 1505 m), (LV27-2) middle part of the continental slope off Sakhalin Island (waterdepth 1305 m), (B37-07) area of the Paramushir gas anomaly (waterdepth 790 m). (–) no data.

* Determined by S.A. Gorbarenko (Pacific Oceanological Institute).

** The mineral composition of carbonate-barite inclusions is based on the XRD, SEM, and optical microscopy data.

variability and complexity (Fig. 3). The cross-cutting of tubular bodies shows the following features: (1) the presence of concentric-zonal structure expressed in different types of mineralization; (2) the presence of the central channel, less than 1 mm (normally 0.5–0.8 mm) in diameter, around which the tubular bodies are formed (Fig. 4a); (3) the tubular bodies are complicated by numerous side channels, less than 1 mm in diameter, which pierce the tubes at different angles and in different directions (Figs. 3, 4a); (4) the internal cavity of channels can be hollow or filled with calcite, barite, calcite-barite, or barite; (5) the presence of concentric brown-gray haloes of organic matter around the channels; and (6) all conceivable tubular bodies contain a significant quantity of clay-clastic particles, which testify to their formation in a sedimentary sequence. Depending on the combination of features listed above, one can distinguish the following principal mineralogical-morphological varieties of the tubular bodies.

Azonal tubular calcite bodies (type Tc₁) are rarely encountered at the level of 45–65 cm. A concentric thin rim of brown-gray color (owing to pigmentation with organic matter) is developed around the central channel within the massive cryptocrystalline calcite material. The channels are normally hollow, and only the finest (0.1 μm) spicular crystals of barite are observed on their walls. Channels walls in some tubes are covered with aggregates of Mg-calcite crystals. Many channels are partially filled with numerous, oval—rounded, carbonate-free clay lumps which are products of the living activity of bottom burrowing organisms (coprolites). The coprolites, in turn, serve as crystallization nuclei for Mg-calcite. Based on the SEM data, Mg-calcite crystals, which fill different cavities and channels in the tubular bodies, represent a complex polycrystalline feature. They consist of numerous scaly-wedgelike crystallites (less than 0.01 mm in size) oriented along a single plane and finally forming relatively large aggregates (0.03–0.05 mm in size), whose habit is similar to that of

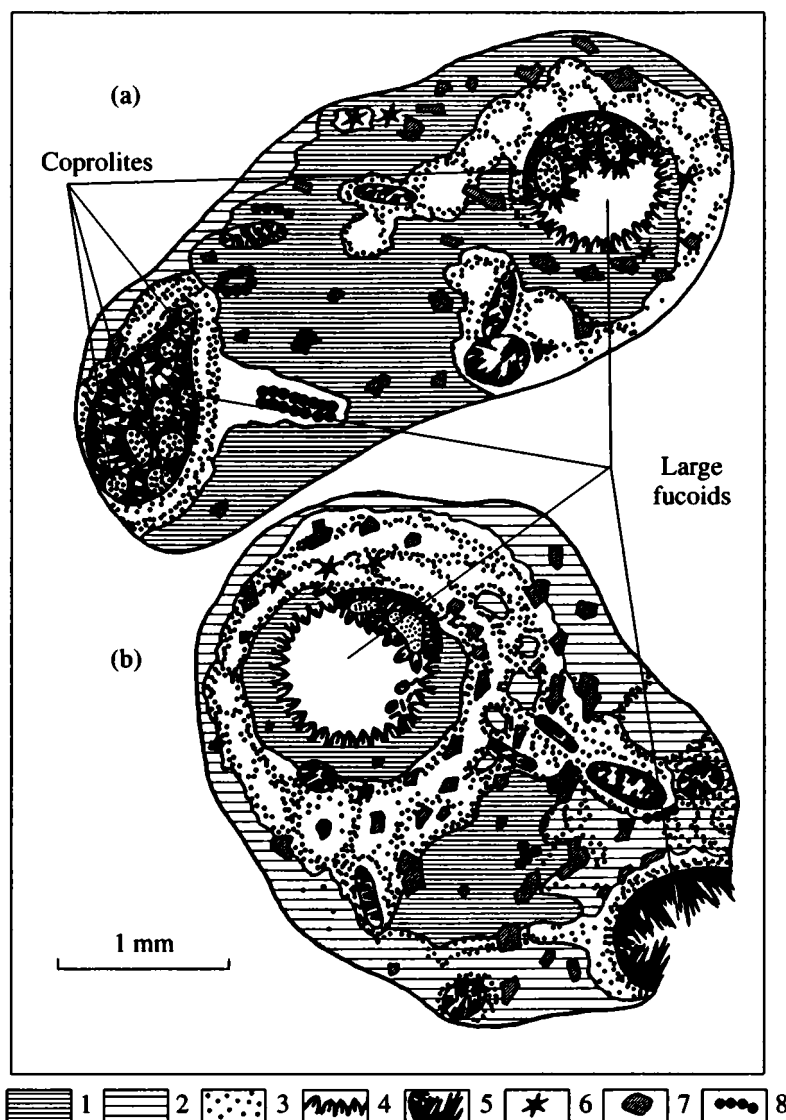


Fig. 3. Internal structure of tubular calcite-barite bodies (type Tc_3). (1) Compact cryptocrystalline Mg calcite cement in clastic-clay sediment, (2) the same but with more rare Mg-calcite mineralization, (3) gray-brown concentric segregations of organic matter in cryptocrystalline barite cement of sediment, (4) druses of Mg calcite crystals on walls of channels, (6) individual barite crystals (fragments of barite "smokers"), (7) sand-sized terrigenous clasts; (8) framboidal pyrite segregations along walls of small channels.

separate crystallites of Mg-calcite (Figs. 4b, 4c). Analogous aggregates (polycrystals) of Mg-calcite, which fill minor channels in the tubular bodies, often occur in the neighbourhood with barite crystals with an ideal lamellar habit. The barite crystals fill free pore space inside the channels (Figs. 4b, 4c, 4e), or they pierce (grow through) calcite crystals without any evident disturbances of their structure (Fig. 4d).

Tubular bodies with concentric-zonal structure (Tc_2) are one of the most widespread types of authigenic newly formed species in the core, but they are most often encountered at the level of 55–80 cm. The bulk of these tubular bodies is composed of a carbonate material. Their central part has a hollow channel, whose walls are incrustated by Mg-calcite crystals.

Along the channel walls in some samples, one can see small aggregates of spicular-lamellar barite crystals, on which larger Mg-calcite crystals grow. In this case, barite serves as a crystallization nucleus for Mg-calcite. The channel is successively overgrown with a compact calcite and carbonate-free sediment with cryptocrystalline barite inclusions. The thickness of this rim is 0.5–2 mm or more. The solid carbonate material appears again on the external surface of the tubes.

Complex tubular bodies with several large channels and different mineral infilling (Tc_3). They are also clearly characterized by the concentric-zonal structure, in much the same way as Tc_2 type tubes (Fig. 3). Here, the inhomogeneous calcite-barite mineralization also

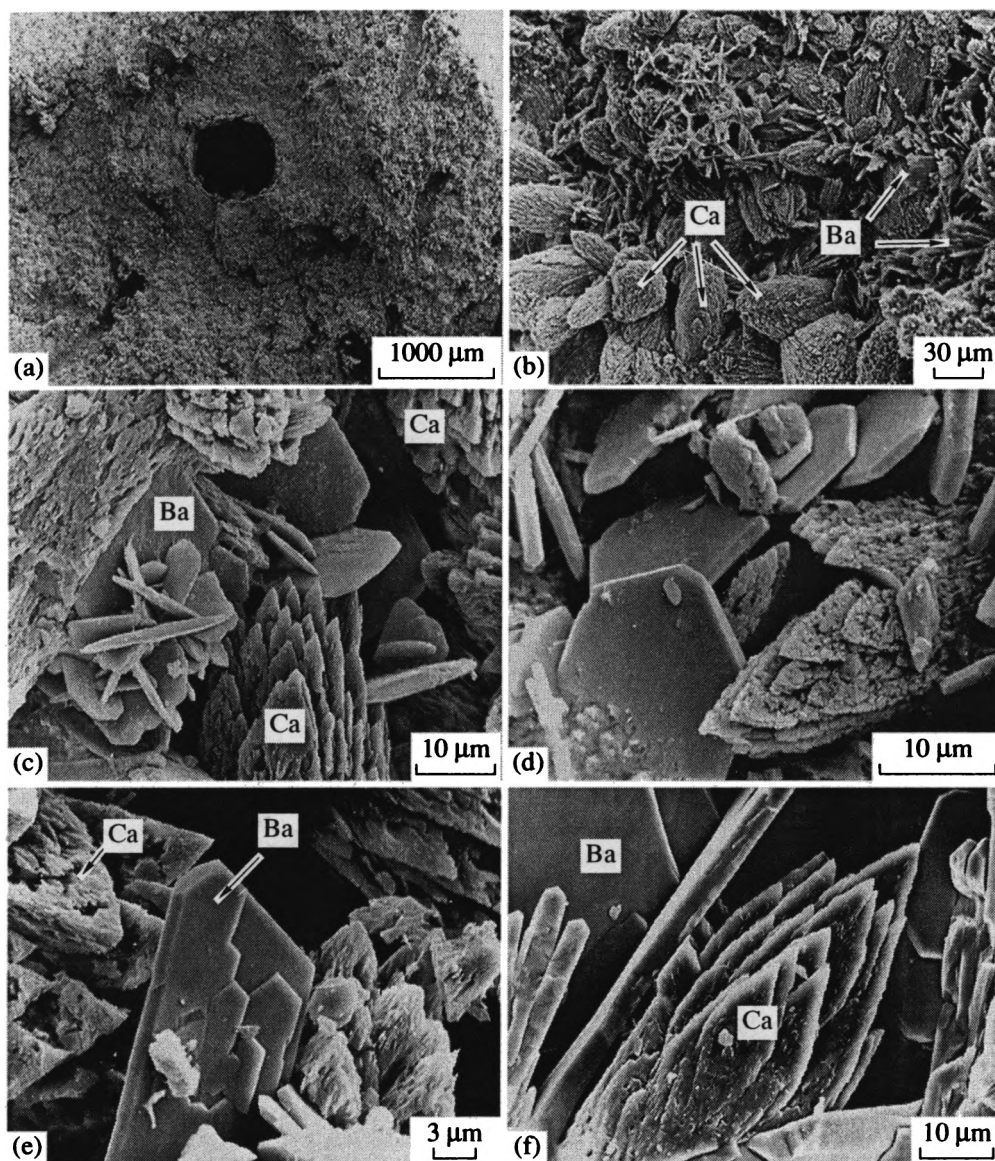


Fig. 4. SEM photomicrographs of calcite-barite bodies in sediments of the Deryugin Basin, Station 9310. (a) General view of the transversal section of a calcite-barite tubular body with well-expressed central channel and smaller transversal channels oriented in different directions; (b) elongated-lamellar and (c, d, e) tabular barite crystals (Ba) among lamellar wedge-shaped aggregates of Mg-calcite crystals (Ca) on walls of channels of calcite-barite tubular bodies; (f) infilling of channels and hollows with Mg-calcite and barite in massive calcite concretions.

impregnates the initial clastic-clay matrix of sediment. Fragments of terrigenous material (quartz, plagioclase, and others) are chaotically distributed through the entire volume of the tubes, although one can occasionally notice some ordered concentric distribution of these particles around the central channels (Figs. 3a, 3b). This may testify to the squeezing-out of clastic particles in soft unconsolidated sediment during the formation of the channels by bottom burrowing organisms. Several channels of different orders are seen within a small area (3×7 mm) of the tube section (Figs. 3a, 3b). One of the large channels is almost completely surrounded by a compact calcite material (the

first calcite rim). The latter, in turn, is surrounded by a continuous rim, 0.5 to 1.5 mm wide, represented in general by the carbonate-free sediment with an admixture of cryptocrystalline, acicular barite crystals, which includes small oval patches of dispersed calcite mineralization. The same area incorporates several thinner channels, which are oriented in different directions and filled with barite crystals. Additionally, rare pyrite framboids are encountered along the walls. The carbonate-free rim of one of the walls of the central channel cuts the calcite material and directly abuts on its walls, slightly deforming and shifting them toward the central part of the channel. Aggregates of lamellar-spicular

barite crystals were formed in this pore space left after the deformation. The barite domain clearly coincides with the boundary between the carbonate and carbonate-free rims (Fig. 3b). Internal walls of the central channel are incrustated by calcite crystals, including barite mineralization in the deformed area. Several concentric rims with pointed pigmentation by organic matter are also clearly expressed around the central channel. One of them is easy to trace along the boundary between the carbonate and carbonate-free rims. The calcite mineralization, not so intensive as in the central part, again develops in the external shell of tubular bodies. The grain margin includes a fragment of one more large channel (comparable in rank with the central channel) completely filled with platelike druses of barite crystals (Fig. 3a). A brown-gray halo of organic matter is also observed around the channel.

The second fragment of a tubular body (Fig. 3b) is essentially identical to that considered above. The only difference is that walls of the central channel are partially incrustated by Mg-calcite crystals (on the carbonate shell side) and partially by barite (on the barite shell side). Barite covers not only the channel walls but also the adjoining coprolites. The second large channel is completely filled with coprolites and platelike druses of barite crystals, and the organic matter halo is well seen. In this case, the coprolites serve as crystallization nuclei for barite. Tiny barite needles are observed here in the carbonate-free material.

Complex tubular bodies are also represented by a relatively rare variety. Walls of the central channel, which pierce the calcite material in such bodies, are completely incrustated by platelike druses of barite crystals (type Tc₄).

Tubular barite bodies were found in all horizons of the core. They differ from other tubular bodies by a lesser size. Their diameter varies from 0.1 to 3 mm (commonly 0.2–0.8 mm); the length is 0.3–10 mm, more rarely up to 15–20 mm. They have a variable shape (spindlelike with a thickening in the center, pear-shaped, sinuous-wormlike, etc.). The tubes are compact and dark gray colored, sometimes with a greenish tint. Their surface is rugged due to abundant inclusions of terrigenous clastic particles. As a rule, central channels are obscured on the external side of the tubes, but are well seen on a fracture. Usually, they are tightly filled with spherical accretions of lamellar yellowish brown barite (Fig. 5a). The tubes can be divided into two varieties: purely barite (type Tb₁) and barite with a thin (external) calcite shell (type Tb₂). Their internal structures are similar: the central channel filled with barite is surrounded by a homogeneous clastic-clay sediment with the spicular cryptocrystalline barite. The barite crystals are larger in voids and microfractures. They form here radiate-spherulitic aggregates with a characteristic fan extinction under crossed nicols. Framboidal pyrite is locally observed along void margins.

Large tubular barite bodies, up to 15–20 mm across and 50 mm long, significantly differ from the ordinary variety. Thinner calcite-barite tubes are associated with clastic particles on the external walls. The tubes can be divided into two types: (1) hollow tubes with thin barite or barite-calcite walls with the interior zone by tightly accreted, spheroidal aggregates consisting of lamellar, yellow barite crystals (type Tb₃); (2) tubes, completely filled with aggregates of barite crystals of different shapes (type Tb₄). The internal space contains diverse barite crystals and their intergrowths. Only some of them are presented in this work (Figs. 5b, 5c, 5d). Druses of dendritic aggregates of yellowish white barite crystals (barite roses) or spheroidal aggregates of lamellar crystals are developed along the walls. They are often covered by a thin coating of tiny barite crystals, which, in turn, are overgrown with new portions of large barite rosettes. The remaining pore space is decorated with an intricate network of very fragile barite crystals arranged in the form of curved columns, pillars, and straight arches (Figs. 5c, 5d). They were probably formed from residual (depleted) solutions retained in the free pore space. The presence of several coatings and intricate barite network can suggest a repeated processing of fluids with Ba-saturated solutions.

Soft calcite concretions (type Cc₁) with a size of 15–20 mm and smooth edges are found only at the level of 5–15 cm. Fractures of the concretions reveal numerous, elongated and differently oriented channels (less than 1 mm in diameter) that pierce the body of concretions. The channels are hollow or more rarely are filled with Mg-calcite crystals.

Massive calcite-barite concretions (type Cc₂), 20–60 mm across, have a flattened shape with some ledges (15–25 and 95–110 cm intervals). Their internal structure is inhomogeneous. Against the gray background of calcite material, some concretions reveal dark gray, oval halo with a diameter of up to 5 mm and spots of brownish gray organic matter on the border. Based on the microscopic study of thin sections, carbonate mineralization is absent inside these haloes but barite impregnation is encountered. In some concretions, inside the barite impregnation halo, one can observe channels (less than 1 mm in diameter) completely filled with druses of lamellar barite crystals. In the concretion sample taken from the level of 15–25 cm, we found that the plane of thin section crossed the oblique section of one of the channels, whose barite- and calcite-impregnated sides are incrustated by barite and calcite crystals, respectively. The boundary between the two walls strictly corresponds to the boundary between two types of mineralization. Compact oval concretions from the 80–85-cm interval (type Cc₃) are compositionally very similar to the previous ones. However, the barite impregnation haloes are absent in them, and their surface is mottled with small channel and pores, part of which is filled with druses of barite and Mg-calcite crystals that are morphologically identical to the crystals from the tubular bodies (Fig. 4f).

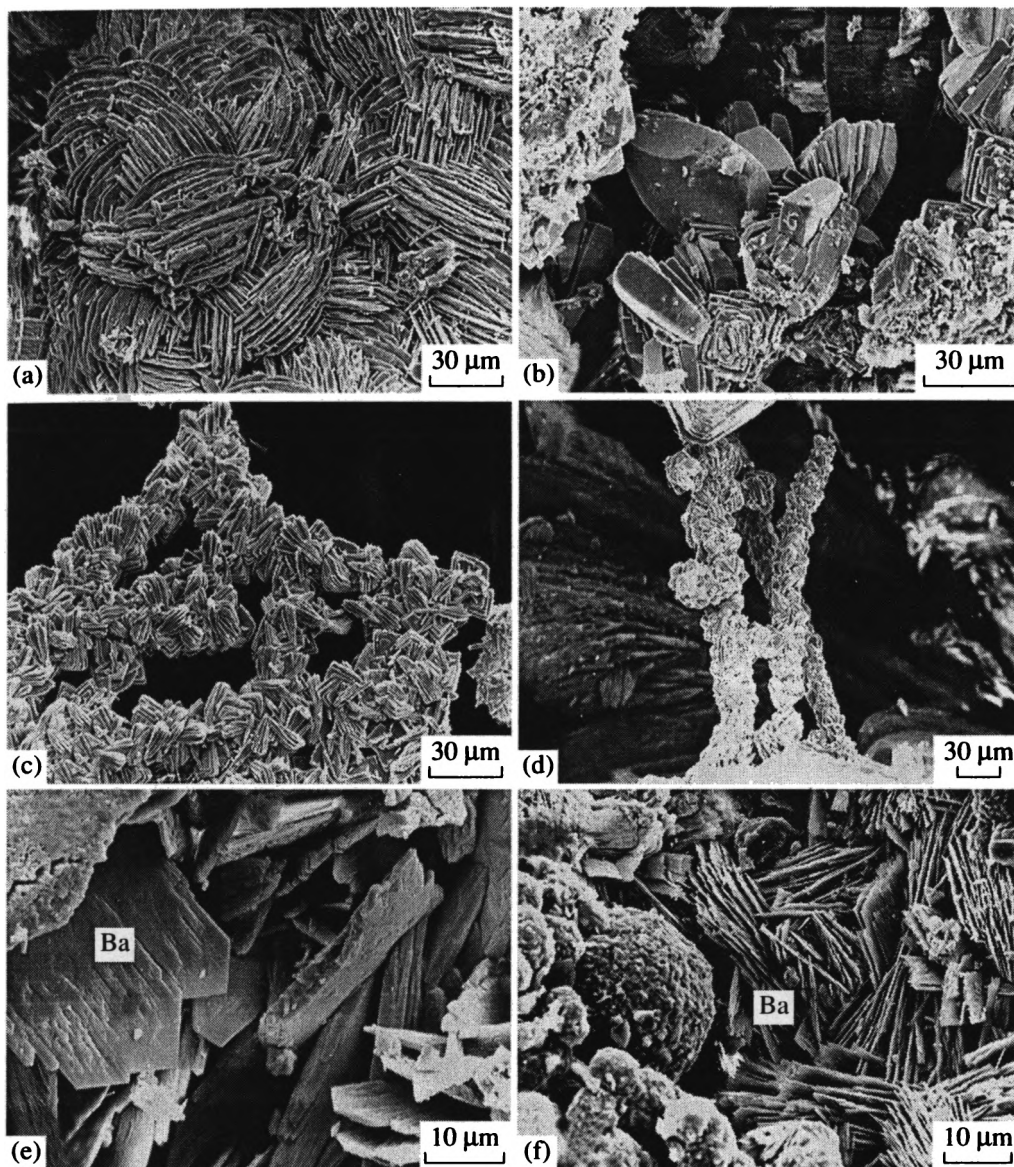


Fig. 5. SEM photomicrographs of barite from tubular bodies in sediments of the Deryugin Basin, Station 9310. (a, b) The most typical shapes of barite crystals filling internal channels and hollows of barite tubular bodies; fragments of (c) barite nets and (d) pillars, developing in hollows of channels of large, tubular barite bodies; chaotically oriented aggregates of (e) wedge-shaped-lamellar and (f) spicular-lamellar barite crystals in the intergranular space of sediments.

Barite in sediments from Station 9310 are found not only in the composition of the above considered tubular bodies and concretions but also in the form of simpler independent bodies. Barite inclusions, 0.01–0.2 mm in size (sometimes larger), are dispersed throughout the entire core. They are represented by very fragile (type Ba_1) segregations, i.e., flipper-shaped, wing-shaped, lenslike, wedgelike and dendritic crystals (Figs. 6a, 6b) and their intergrowths (type Ba_2) of cloudy white or pale yellow color (Figs. 6c, 6d, 6e). They are mostly clasts of larger fragments of pure, highly porous barite that makes up the buildups rising 3–10 m above the seafloor. This buildups (barite “smokers”) were formed in

the areas of direct seepages of Ba-saturated fluids through the seafloor above the sediment/water interface. Buildups of barite “smokers” were found in abundance during the detailed investigations of the rise with the use of a underwater towed TV camera (OFOS) and dredging on the 28th Cruise of the R/V *Akademik Lavrentyev* in 1998 during the expedition within the Russian–German KOMEX Project (Cruise ..., 1999).

Barite formed in the intergranular space of sediments has a specific morphology (type Ba_3). It is represented by barite beads with an ideal spherical shape, 0.1–0.8 mm in size, sometimes microconcretions up to 2 mm (Fig. 7a), or chaotic aggregates of spicular-lamel-

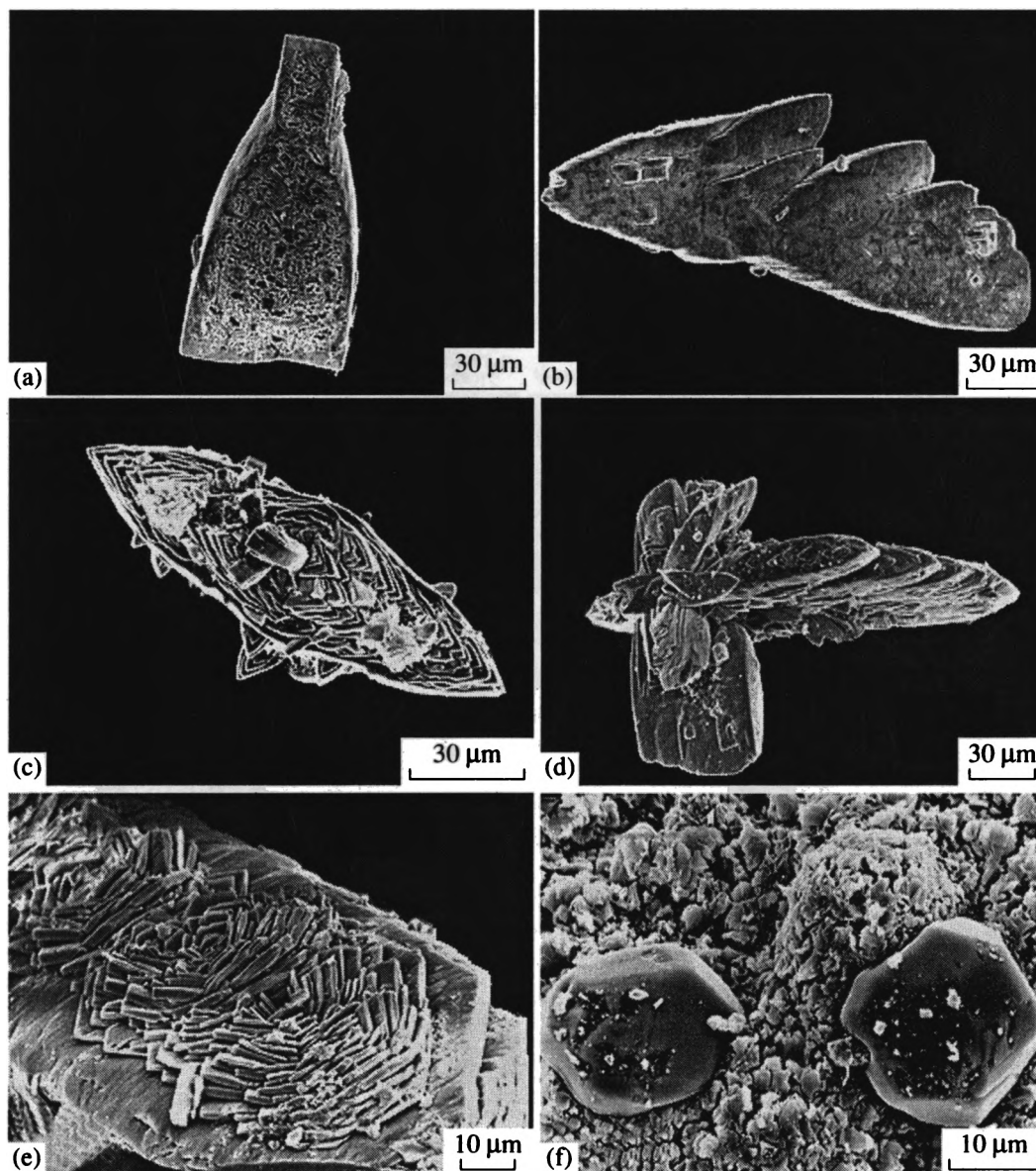


Fig. 6. SEM photomicrographs of edaphogenic barite (fragments of barite “smokers”) in sediments of the Deryugin Deep, Station 9310. (a) Flipper-shaped and (b) wing-shaped barite crystals; (c, d, e) complex aggregates of barite crystals; (f) idiomorphic native sulfur crystals on the surface of pyrite tubes.

lar crystals in hollows and small channels (Figs. 5e, 5f). The microscopic study of sections and SEM data showed that microconcretions (spherulites) are represented by tightly accreted spicular and lamellar crystallites of barite (Figs. 7c, 7d, 7e). In most cases, the distinct nuclei of crystallization are not expressed. An alternative to these nuclei is sometimes represented by formless, brownish gray clay lumps, probably enriched in organic matter or radiolarian shells. In the course of their growth, barite spherulites captured numerous inclusions of clay and clastic particles, and the particles are often projecting above the spherulite surface (Fig. 7e). Purer barite aggregates without evident inclusions of clastic particles can be situated inside the

spherulites. Additionally, one can see tight spherulite aggregates with several crystallization centers, inside which framboidal pyrite accumulations can occur. A part of the spherulites has a concentric-zonal pattern testifying to several stages of barite formation (Fig. 7c). The grains with more complex morphology belong to the same type of the authigenic-diagenetic barite mineralization. The crystallization nuclei in them are generally represented by different porous (mostly organic) remains: fragments of chitin shells of bottom burrowing organisms, wood, pyrite tubes, and sometimes fragments of larger tubular barite bodies (Figs. 7a, 7b). Barite aggregates with a sophisticated shape originate in the process in the form of incrustated fringes with a

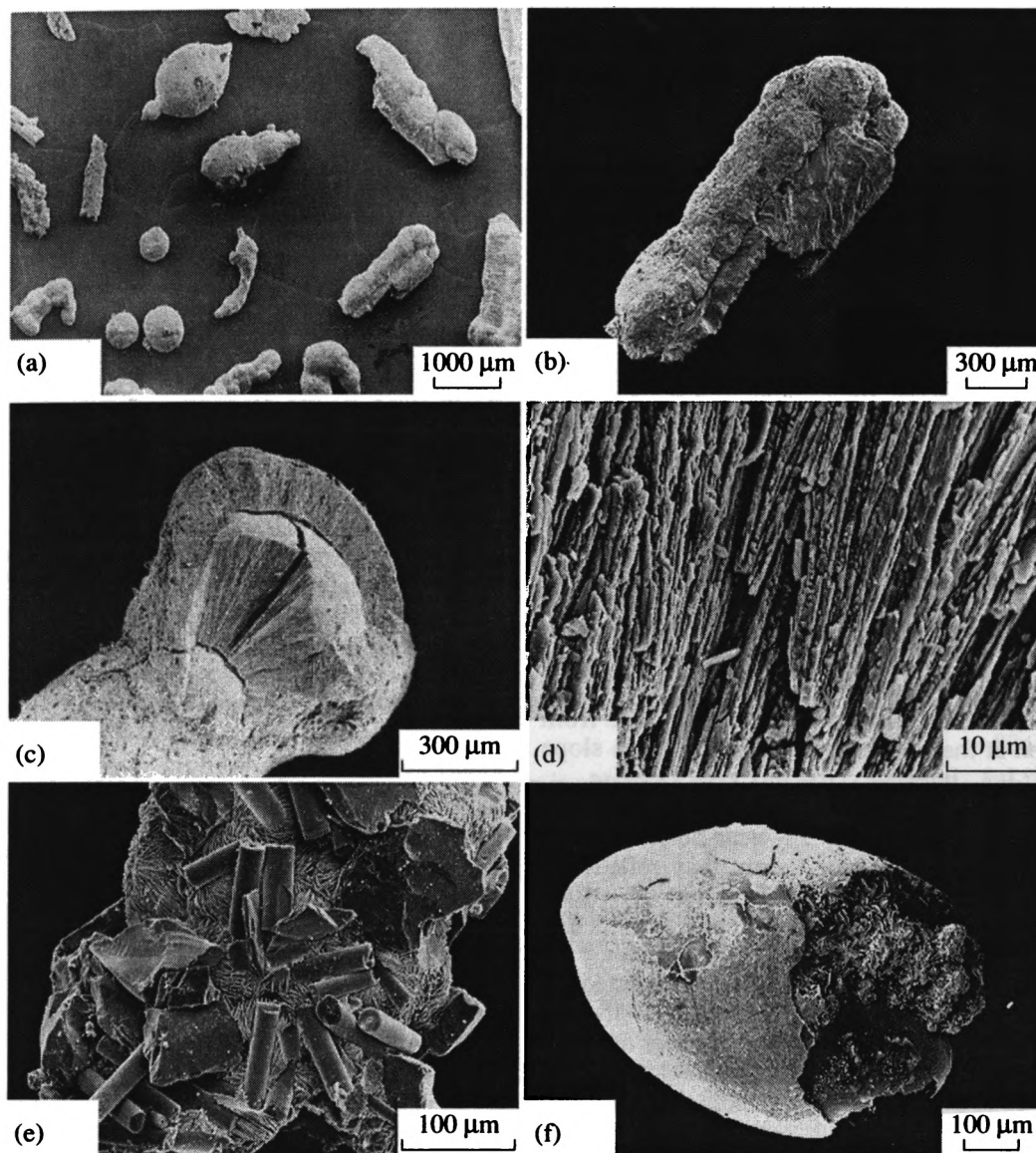


Fig. 7. SEM photomicrographs of authigenic-diagenetic barites in sediments of the Deryugin Deep, Station 9310. (a) Barite beads (microconcretions) and barite overgrowth on organic remains; (b) lamellar barite crystals overgrowth on the chitin shell of a tube-worm (enlarged part of Fig. 7a); (c) concentric-zonal structure of barite microconcretions; (d) the same, enlarged part: concentric layers consist of small spicular-lamellar barite crystals; (e) cementation of clastic particles (quartz and fragments of siliceous sponge spicules) with aggregates of lamellar barite crystals; (f) barite-filled shell of a benthic foraminifer.

spherulitic structure, rims around organic particles, and chains of tightly accreted small spheres perched on a single axis, which is represented by thin and long fragments of tubeworms (pogonophors). In the remains of brown-colored chitin shells within the tubeworms, the interior walls are covered by framboid pyrite accumulations, and the central part is incrustated by tight spherulite aggregates of probably the early generation of barite. Pseudomorphs of barite developed upon shells of benthic and planktonic foraminifers are sometimes observed in addition to the varieties listed above (Fig. 7f). The authigenic spherical barite and its more

complex morphological types are most abundant in the lower part of the core, below the level of 85 cm.

In addition to the authigenic barite and carbonate, pyrite is also abundant (up to 37 wt % of the heavy fraction) in sediments from Core 9310 and is represented by predominantly elongated, wormlike tubes with a diameter of 0.03–0.1 mm.

ISOTOPE DATA

Some idea of the source of mineral-forming components and the conditions of barite and carbonate forma-

tion can be obtained from the isotope date on oxygen, carbon, sulfur, and strontium.

The studied carbonate from Core 9310 is characterized by rather stable values of carbon isotopes. The values of $\delta^{13}\text{C}$ fall within a range of -37.6 to -42.3‰ PDB and agree well with isotope values for carbonates from other regions of the World Ocean related to the known seeps of cold gas-saturated fluids on the seafloor (Lein *et al.*, 1989; Ginsburg and Solov'ev, 1994; Ritger *et al.*, 1987; Kulm and Suess, 1990; Paull *et al.*, 1992; Sample *et al.*, 1993; Roberts and Aharon, 1994; Von Rad *et al.*, 1996; Bohrmann *et al.*, 1998; Suess *et al.*, 1998, and others). As is well known, carbonates inherit the carbon isotopic composition, which is established in pore waters after the achievement of oversaturation with carbonate ions (Roberts and Aharon, 1994). Data on the carbon isotopic composition in carbonates from Core 9310 suggest that the anaerobic oxidation of methane was the principal mechanism of carbon dioxide supply during their formation. This process was responsible for the formation of Mg-calcite depleted in $\delta^{13}\text{C}$ (Table 1). For comparison, we analyzed the carbon isotopic composition in mollusk shell fragments (Station 9310, interval 15–25 cm) and diagenetic calcite crystals from the core taken at the base of the Deryugin Basin slope (Station LV27-2, interval 570–580 cm) (Cruise ..., 1997). In the first case, the isotope values correspond to usual cold water conditions of near-bottom water ($\delta^{13}\text{C} = -3.79\text{‰}$). In the second case, they reflect the microbiological decay of organic matter in sulfate reduction zone ($\delta^{13}\text{C} = -16.58\text{‰}$). The plot of $\delta^{13}\text{C}$ distribution over the core reveals the following trend: the carbon isotopic composition becomes heavier from lower horizons (-42.86‰) to the intermediate (45–55 cm) horizon (-37.59‰), and then becomes lighter again in the upper horizon (Fig. 2). It is noticeable that the heaviest values of the isotopic composition fall approximately on the Holocene/Pleistocene boundary. For other regions, it was established that one of the reasons for $\delta^{13}\text{C}$ variations may be a heterogeneity of the mineral composition of carbonates (the presence of aragonite, Mg-calcite, and dolomite) (Kulm and Suess, 1990; Jorgensen, 1992; Matsumoto, 1992; Sample *et al.*, 1993; Roberts and Aharon, 1994; Bohrmann *et al.*, 1998). However, changes in the mineralogy of carbonates in Core 9310 are moderate and, therefore, cannot explain the above $\delta^{13}\text{C}$ distribution. One can suppose that such variations in $\delta^{13}\text{C}$ are caused by the intensity of microbial methane oxidation. It was established that the CO_2 concentrations in pore water is inversely correlated with the $\delta^{13}\text{C}$ value (Goldhaber and Kaplan, 1974; Brumsack *et al.*, 1992; Matsumoto, 1992; Paull *et al.*, 1992). The sulfate-reducing activity of bacteria and decay of organic matter, which comes to the seafloor, also can contribute some amount of carbonate ions to pore water. But, because $\delta^{13}\text{C}$ values in organic matter are somewhat heavier, relative to those in the methane source, the registered variations in the content of stable carbon isotope in carbonates from Core 9310 may be

caused by the mixing of these two sources of carbon to sediments. In this case, the slightly heavier values of $\delta^{13}\text{C}$ in carbonates from the Holocene/Pleistocene boundary horizon (Fig. 2) can be attributed to an increase in the biological productivity of seawaters at that time and the consequently maximal input of organic matter to the seafloor (Gorbarenko, 1991, 1996).

Oxygen isotope values in carbonates from Core 9310 change within a narrow range, from 3.83 to 4.89‰ PDB (Table 1), and are also in good agreement with similar carbonates from cold fluid seeps in other regions of the World Ocean (Kulm and Suess, 1990; Paull *et al.*, 1992; Roberts and Aharon, 1994; Bohrmann *et al.*, 1998; Suess *et al.*, 1998, and others). Variations in the $\delta^{18}\text{O}$ distribution are noted throughout the core (Fig. 2), and they have a high negative correlation with $\delta^{13}\text{C}$. As noted above, the mineral composition of carbonates cannot be responsible for the isotopic composition variation throughout the core, although the validity this factor was convincingly demonstrated for several carbonate concretions and crusts from bottom sediments on the continental margins of Cascadia (Oregon), the Gulf of Mexico (Kulm and Suess, 1990; Roberts *et al.*, 1990; Roberts and Aharon, 1994; Bohrmann *et al.*, 1998), and from sediments of the Baltic Sea (Jorgensen, 1989). In contrast to sediments from these regions, carbonates of the studied core are dominated by Mg-calcite. The enrichment of Station 9310 carbonates in heavy oxygen isotope immediately rules out the influence of hydrothermal fluids on the formation of these carbonates (Astakhova *et al.*, 1987, 1990). This is also testified by the direct correlation between $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, which also rules out the influence of hydrothermal fluids (Sample *et al.*, 1993). Values of $^{87}\text{Sr}/^{86}\text{Sr}$ in carbonate-barite formations from Core 9310 range from 0.708619 to 0.708726 (Tables 1, 2), which are lower than the isotope value for seawater (Capo and DePaolo, 1990). For example, Sample *et al.* (1993) demonstrated that some carbonates in sediments on the continental margin of Cascadia were formed with the involvement of fluids with low values of $\delta^{18}\text{O}$ but high contents of radiogenic Sr, suggesting the participation of hydrothermal solutions in the alteration of clay minerals in the sedimentary sequence at a great depth.

Considering that authigenic carbonates are formed near the seafloor, it is evident that changes in $\delta^{18}\text{O}$ in Core 9310 can be explained by variations in near-bottom water temperature owing to changes in paleogeographic conditions of sedimentation during the Late Pleistocene–Holocene. The hypothesis of gas-hydrate destabilization due to temperature increase in the near-bottom water during the glacioeustatic sealevel fall in the Late Pleistocene and the consequent appearance of heavy $\delta^{18}\text{O}$ values in carbonates (Bohrmann *et al.*, 1998) seems to be invalid for carbonates from the Deryugin Basin. A substantial temperature rise is hardly possible at such water depths (> 1500 m).

Table 2. Values of oxygen and sulfur isotopes and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in barite from sediments of the Deryugin Basin (Sea of Okhotsk)

Station number and horizon, cm	Type of barite inclusions	$\delta^{18}\text{O}$, ‰ PDB	$\delta^{34}\text{S}$, ‰ CTD	$^{87}\text{Sr}/^{86}\text{Sr}$
9310 (5–15)	Barite tube filled with lamellar barite crystals (type Tb ₁)	+16.4	+70.3	–
9310 (15–25)/1	Barite tube, 1.5–12 mm in size (type Tb ₁)	+22.8	+61.6	0.708763
9310 (15–25)/2	Massive calcite concretion with barite inclusion (type Cc ₂)	+22.5	+64.5	0.708762
9310 (35–45)/1	Yellow barite crystals from a large (15–30 mm) barite tube (type Tb ₄)	+10.9	+24.9	0.708518
9310 (35–45)/2	Barite tube (2.5–4 mm) filled with barite crystals (type Tb ₁)	+19.9	+61.0	0.708749
9310 (35–45)/3	Yellow barite crystals from a large diameter barite tube (type Tb ₄)	+11.7	+24.9	0.708527
9310 (45–55)/1	Fragment of a large diameter barite tube with druse of lamellar barite crystals (type Tb ₃)	+10.6	+30.0	0.708512
9310 (45–55)/2	Type Tb ₃	+16.9	+57.4	0.708632
9310 (55–65)/1	Fragment of complex calcite–barite tube, 40–80 mm in size (type Tc ₂)	+24.7	+80.1	0.708711
9310 (55–65)/2	Type Tc ₂	+15.4	+39.3	0.708474
9310 (65–80)	Calcite–barite tube (type Tc ₂)	+16.3	+70.6	–
9310 (80–85)	Fragment of massive calcite concretion (40–60 mm) with small channels filled with barite (type Cc ₃)	+20.8	+67.0	0.708674
9310 (85–95)	Barite tube completely filled with barite crystals (type Tb ₁)	+15.3	+72.9	–
9310 (95–105)	The same	+17.3	+80.9	–
9310 (105–115)	Barite beads (microconcretions), 0.3–1.5 mm in size (type Ba ₃)	+19.0	+56.3	0.708693

Note: (–) no data.

It is known that sulfate-reducing bacteria utilize light sulfur isotope and, consequently, the remaining sulfate is enriched in ^{34}S (Mizutani and Rafter, 1973). In this case, diagenetic barite formed in the sedimentary sequence should be isotopically heavier than the seawater (Goldhaber and Kaplan, 1980; Von Breyman *et al.*, 1992; Torres *et al.*, 1996b). Our $\delta^{34}\text{S}$ data (Table 2) do not contradict this inference. The $\delta^{34}\text{S}$ values in barites from Core 9310 range from 24.9 to 80.1‰ CTD. Maximal values of $\delta^{34}\text{S}$ are typical of complex barite–calcite inclusions (type Tc₂) that are abundant at the level of 55–80 cm. At other levels, the tubular barite bodies, calcite concretions with inclusions of barite, and authigenic barite spherulites (type Ba₃) have approximately equal values of $\delta^{34}\text{S}$ (57.3–64.5‰ CTD), probably suggesting similar conditions of their formation. Special attention must be given to the fact that a part of the samples is less enriched in ^{34}S (24.9–39.3‰ CTD), approaching the value of $\delta^{34}\text{S}$ for seawater. All these samples are represented by fragments of large tubular barite bodies with a diameter of 1.5–2.0 mm (type Tb₄). It is possible that these bodies were formed with the participation of both the residual sulfate from pore water of sediments and the seawater-derived, $\delta^{34}\text{S}$ -depleted sulfate that partially infiltrated in these tubular bodies. However, the small barite tubes (type Tb₁), taken from the same level, showed a sharp increase in $\delta^{34}\text{S}$ values up to 61‰ CTD (Table 2). The

studied barite samples demonstrate a strong direct correlation between values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$.

CONCLUSION

The carbonate–barite mineralization in sediments from the Deryugin Basin (Station 9310) is presumably related to the percolation of cold methane-bearing fluids coming up from deep levels of the sedimentary cover along fault zones.

Carbonates were predominantly formed during the anaerobic microbial oxidation of methane, which is present in the composition of fluids. The data on the isotopic composition of oxygen and carbon correlate well with the values typical of carbonates from other regions of the World Ocean pertaining to the submarine venting of cold gaseous fluids (Lein *et al.*, 1989; Ginsburg and Solov'ev, 1994; Ritger *et al.*, 1987; Kulm and Suess, 1990; Paull *et al.*, 1992; Sample *et al.*, 1993; Roberts and Aharon, 1994; Von Rad *et al.*, 1996; Bohrmann *et al.*, 1998; Suess *et al.*, 1998, and others). The strontium and oxygen isotopy data rule out any influence of hydrothermal solutions, which were involved in the alteration of clay minerals of the sedimentary sequence and basement rocks, on the formation of carbonate–barite bodies.

According to our data, carbonates are formed in the immediate vicinity of the seafloor. Soft unconsolidated

concretions are encountered already at the level of 5–15 cm. It is not improbable that carbonate crusts may exist on the seafloor. The crust is an obligatory feature of the areas where cold, gas-saturated fluids percolate through seafloor sediments. Small (1.5–2 cm) flattened fragments (with a CaCO_3 content up to 78.6%) taken during the dredging of slopes of the rise (Astakhova *et al.*, 1990) are likely to be remnants of such crusts and plates.

The majority of carbonate and calcite–carbonate accumulations found at Station 9310 is represented by tubular bodies with variable shape and mineral composition. The microscopic study of their internal structure testifies to their biological origin. They are chiefly fucoid remains in the sediment pertaining to mollusks, pogonophores, polychaetes, etc., i.e., the community that intensively develops on the seafloor in fluid seepage zones (Embley *et al.*, 1990; Kulm and Suess, 1990; McDonald *et al.*, 1990; Paull *et al.*, 1992; Roberts and Aharon, 1994; Barry *et al.*, 1996; Sibuet and Olu, 1998; Suess *et al.*, 1998). The channel hollows (fucoids) are an ideal reservoir for pore water and ascending fluids. Naturally, methane also can accumulate in this free pore space. As a result of the methane-oxidizing activity of bacteria, carbonate crust can form around these channels. When the conditions of oversaturation are achieved, Mg–calcite precipitates and cement the host sediments. However, it is not as yet possible to quantitatively estimate this process.

We propose the following model of barite formation in the Deryugin Basin. It was probably related to the remobilization of biogenic Ba below the sulfate depletion zone and its subsequent transportation by ascending fluids to upper layers of the sedimentary cover (Von Breyman *et al.*, 1992; Torres *et al.*, 1996b). It is known that a large flux of labile Ba produced by organisms in seawater is necessary for the formation of barite (Stroobants *et al.*, 1991; Dehairs *et al.*, 1991). The primary source for Ba are barites that are present in the composition of organic matter, primarily siliceous biogenic organisms (Gurvich *et al.*, 1978; Stroobants *et al.*, 1991; Dehairs *et al.*, 1991; Dymond *et al.*, 1992), which are abundant in the Sea of Okhotsk (Koblents-Mishke, 1967; Bogorov, 1974). During the burial and subsequent decomposition of this matter, the dissolved Ba accumulates in sediments below the sulfate reduction zone.

All barite samples from the studied sediments are characterized by $\delta^{34}\text{S}$ values that are higher than those for seawater. This may be evidence of diagenetic fixing of barite in the sulfate reduction zone by residual sulfate enriched in the heavy sulfur isotope (Mizutani and Rafter, 1973; McCready and Krouse, 1980). The question remains to be answered about the timing of barite formation. As stated above, the studied core including various morphological forms of barite embraces a time span of more than 20 ka. We can suggest two possible ways of barite formation: a continuous process of barite

formation with the migration of the “barite front”, as new sediment layers accumulate, or the barite formation within the narrow belt of a permeable fracture zone along the pathway of Ba-saturated fluids migration. It was established that the formation of thin barite crust (~2 cm) in the “barite front” takes a long time (Von Breyman *et al.*, 1992; Torres *et al.*, 1996b). The second way of the barite formation at Station 9310 in the Deryugin Basin seems to be more preferable. This is also testified by hummocks, up to 10 m high, discovered there during the underwater TV (OFOS) survey. Based on dredging data, the hummocks consist of pure, very porous, white barite (Cruise..., 1999). According to Astakhova *et al.* (1990), the BaO content in such barites is 62.27%. Similar accumulations could form only on the seafloor surface above the water/sediment interface when the dissolved Ba from ascending fluids reacts with the sulfate from seawater.

The morphology of pyrite, which is predominantly encountered in the form of elongate wormlike tubes with a diameter of 0.03–0.1 mm, may also be evidence for the percolation and discharge of gas-saturated fluids on the seafloor at Station 9310. The surface of several pyrite grains contains idiomorphic white crystals of native sulfur (Fig. 6f). Such pyrite segregations are pseudomorphs developing on organic remains. Taking into consideration the small size of pyrite tubes, one can suppose that the pyrite partially replaced remains of bacteria *Beggiatoa*, which form bacterial mats in fluid seepage areas (Lein *et al.*, 1989; Roberts *et al.*, 1990; Sassen *et al.*, 1993; Larkin *et al.*, 1994; Roberts and Aharon, 1994, and others). Similar pyritic pseudomorphs of bacteria were reported by Larkin *et al.* (1992) from sediments in the strong fluid activity (cold seep) zone on the continental slope of the Gulf of Mexico.

Thus, based on our investigations, the studied area of the Deryugin Deep incorporates a long-lived cold seep center containing methane and dissolved Ba. Authigenic–diagenetic carbonates and barites are formed in sediments along the periphery. The recent moderate seepage of gas-saturated fluids on the seafloor should not be ruled out as indicated by an anomalous methane concentration in the near-bottom layer of seawater (Cruise ..., 1999). The data obtained, including the isotope evidence and the absence of paragenetic mineral associations that are typical of hydrothermal systems (Khvorova and Serova, 1991; Lisitsyn *et al.*, 1990; Gurvich, 1998, and others) rule out the hydrothermal nature of the carbonate barite mineralization in sediments of the Deryugin Basin.

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Geochemistry of Rare Earth Elements in Ferromanganese Micro- and Macronodules from the Pacific Nonproductive Zone

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Abstract—Ferromanganese micro- and macronodules in eupelagic clays at Site 35 of the South Basin were examined in order to check the REE distribution during the ferromanganese ore formation in nonproductive zones of the Pacific Ocean. We studied host sediments and their labile fraction, ferromanganese micronodules (fractions 50–100, 100–250, 250–500, and >500 μm) from eupelagic clays (horizons 37–40, 105–110, 165–175, and 189–190 cm), and buried ferromanganese micronodules (horizons 64–68, 158–159, and 165–166 cm). Based on phase analysis data, the anomalous REE enrichment of eupelagic clays from Site 35 is related to the accumulation of rare earth elements in iron hydroxophosphates. The Ce concentration, generally linked to manganese oxyhydroxides, is governed by the oxidation of Mn and Ce in oceanic surficial waters. Micronodules ($\text{Mn/Fe} = 0.7\text{--}1.6$) inherit compositional features of the labile fraction of sediments. The Ce, Co, and Th concentrations depend on the micronodule dimension. The enrichment of micronodules in hydrogenic or hydrothermal substance is governed by their dimension and the dominant source of suspended oxyhydroxide material. The study of buried ferromanganese micronodules revealed general regularities in the compositional evolution of oxyhydroxide matrices of ferromanganese micro- and macronodules. The compositional variation of micro- and macronodules, relative to the labile fraction of sediments, in the Pacific nonproductive zone dramatically differs from the pattern in bioproductive zones, where micronodule compositions in larger fractions are similar to those in associated macronodules and labile fractions of the host sediment as a result of the more intense suboxidative diagenesis.

Ferromanganese micronodules are ubiquitous in oxidized pelagic sediments (Addy, 1979; Dubinin and Sval'nov, 1995, 1996, 2000; Kunzendorf *et al.*, 1989; Pattan, 1993; Pattan *et al.*, 1994; Stoffers *et al.*, 1984a, 1985). Their content inversely correlates with the sedimentation rate (Sval'nov, 1991; Sval'nov *et al.*, 1991a). Ferromanganese micro- and macronodules are generally similar in structure, texture, mineralogy, and chemistry, except for some dimensional distinctions and the higher Mn/Fe value in micronodules. Ferromanganese oxyhydroxides, segregations, usually not more than 1000 μm in size, are recognized as micronodules. According to some researchers (Kunzendorf *et al.*, 1989; Pattan, 1993), the size gap between micro- and macronodules is lacking.

The compositional specificity of micro- and macronodules was reported by several researchers (Addy, 1979; Dubinin and Sval'nov, 1995, 1996, 2000; Glasby *et al.*, 1987; Kunzendorf *et al.*, 1989; Pattan *et al.*, 1994). The micronodule composition versus dimension relationship was discussed in our earlier works. In bioproductive zones of the Pacific, the composition of larger micronodules approaches that of the associated ferromanganese nodule and labile fraction of sediments. In suboxidative diagenetic conditions, micronodules are more hydrogenic than nodules. The general compositional trend of micro- and macronodules toward the labile fraction of host sediments suggests that micronodules represent the initial stage of ferro-

manganese mineralization in the ocean (Dubinin and Sval'nov, 2000).

The above conclusions are based on the REE distribution in separate micronodule fractions. It became obvious that rare earth elements are sensitive indicators of material sources. Under conditions of terrigenous material deficit, rare earth elements are fractionated in the ocean water. Compounds of HREE are more stable than their LREE counterparts and are prone to accumulation in the deep-water pelagic zone of oceans. As a result of the Ce oxidation and transition to the suspended form, a negative Ce anomaly can be developed in the ocean water (Bertram and Elderfield, 1993; Klinkhammer *et al.*, 1983; Masuzawa and Koyama, 1989; Sholkovitz *et al.*, 1994; Zhang and Nozaki, 1996). The consequent positive Ce anomaly in the REE signature of suspended material is inherited by hydrogenic ferromanganese nodules and crusts (Aplin, 1984; Courtois and Clauer, 1980; De Carlo, 1991; Dubinin, 1998; Hein *et al.*, 1988; Piper, 1974; Toth, 1980). Therefore, we can assume that the REE signature was least altered in nodules and crusts during the evolution from the suspended particulate to hydrogenic nodules and crusts. Individual REE phases are lacking in ferromanganese sediments, and REE concentrations correlate with Fe contents. Rare earth elements, which are included in iron oxyhydroxides of crusts and nodules (Dubinin and Volkov, 1989), are derived from the ocean water. However, the REE signature depends on the gen-

esis of oceanic oxyhydroxides. Hydrothermal iron oxyhydroxides are characterized by a negative Ce anomaly and LREE deficit (German *et al.*, 1990). Such REE patterns are typical of metalliferous sediments and associated formations (nodules and rapidly growing crusts) that are widespread around hydrothermal vents in the ocean (Burnett and Piper, 1977; Courtois and Clauer, 1980; Dubinin, 1996; Dubinin and Volkov, 1986; Elderfield and Greaves, 1981; Piper and Graef, 1974; Toth, 1980; Volkov and Dubinin, 1987).

The present work is devoted to the distribution of REE and other trace elements in ferromanganese micro- and macronodules in sediments with different hydrothermal admixtures in the nonproductive zone of the Pacific (South Basin). Thus, this work is a continuation of the study of REE geochemistry in nodules versus bioproductivity of surficial waters (Dubinin and Sval'nov, 2000).

MATERIALS AND METHODS

The material was collected by a Piston corer at Site 35 in the South Basin of the Pacific (29°36' S, 149°58' W, depth 3880 m) during cruise 26 of the R/V *Akademik Korolev*. The core (length 190 cm) is composed of coccolith-foraminiferal oozes with small (1–3 cm) ferromanganese nodules from the seafloor surface (horizon 0–10 cm), a ferromanganese crust (10–12 cm), and oxidized eupelagic clays (12–190 cm) with a minor admixture of biogenic carbonate material at some horizons (Fig. 1). The pelitic fraction primarily consists of smectite. Along the entire core, sandy-silty fractions (>50 µm) contain zeolite (phillipsite), bone detritus, and ferromanganese micronodules. Sediments from horizons 64–68, 158–159, and 165–166 cm contain multinucleus ferromanganese nodules, 1–1.5 cm across. The nucleus of one nodule (horizon 158–159 cm) is represented by an oblate material composed of smectite and phillipsite (based on the X-ray phase analysis data).

Zeolites, bone detritus, and micronodules were separated from >50-µm-fractions of four horizons (37–40, 105–110, 165–175, and 189–190 cm) under a binocular microscope. The micronodules were sieved into four fractions (50–100, 100–250, 250–500, and >500 µm). Masses of separate micronodule fractions and their proportion in sediments of four horizons at Site 35 are presented in Table 1. Relationships of micronodule fractions at separate horizons are shown in Fig. 2. It is evident that the micronodule fraction mass depends on the sediment horizon. Micronodules have rounded-angular, angular-rounded, fine-nodular, acicular-spherical, or angular-accretionary forms. The color varies from brown to brownish black and black. The surface is coarse, sparkling, dull, greasy, or sometimes lustrous. The nucleus is composed of lumps of indurated sediment, bone detritus, and zeolite aggregates.

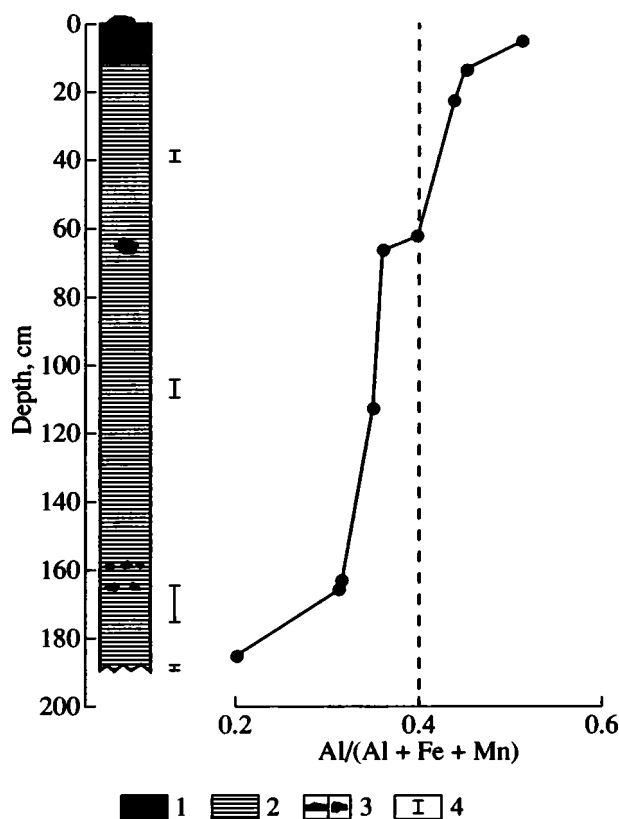


Fig. 1. The $Al/(Al + Fe + Mn)$ vs. depth plot for Site 35 sediments. (1) Carbonate mud; (2) eupelagic clay; (3) Ferromanganese crust/nodule; (4) sampling horizon (fraction >50 µm). The dashed line shows the $Al/(Al + Fe + Mn) = 0.4$ value, below which bottom sediments contain the hydrothermal Fe and Mn (Boström, 1973).

The micronodule samples for chemical analysis were taken from different fractions. However, the >500-µm-fraction from horizons 165–175 and 189–190 cm was not analyzed, because the material was insufficient (Table 1). The quality of the analytical material was checked with a binocular microscope.

Weighed samples (30–50 mg) were treated with an $HF + HClO_4$ mixture in platinum dishes. The manganese(IV) oxide precipitate obtained as a result of the decomposition of ferromanganese nodules and crust was reduced in 10 ml of 6M HCl. Then the sample was transformed to 5% HNO_3 solution and used for the analysis of REE, Mo, W, and Th by the ICP-MS method (Dubinin, 1993; Strekopytov and Dubinin, 1997). Minor elements (Fe, Mn, Co, Ni, Cu, Ca, Ti, and Al) were analyzed in the same samples by the flame spectroscopy version of the atomic absorption method with a reproducibility of 3–5 rel % (N.N. Zavadskaya, the analyst). The P concentration was measured by the photospectrometry based on color intensity of the blue P–Mo–Sb compound (reproducibility 3 rel %).

Element forms were studied on the basis of 1M $NH_2OH \cdot HCl + 25\% CH_3COOH$ (Chester and Hughes,

Table 1. Mass relationships between ferromanganese micronodule fractions and host sediment

Horizon, m	Sediment mass, g	Micronodule fraction											
		> 500 μm			500–250 μm			250–100 μm			100–50 μm		
		mass, g	% of the sedi- ment mass	% of the >50-μm- fraction mass	mass, g	% of the sedi- ment mass	% of the >50-μm- fraction mass	mass, g	% of the sedi- ment mass	% of the >50-μm- fraction mass	mass, g	% of the sedi- ment mass	% of the >50-μm- fraction mass
37–40	10.69	0.0774	0.72	14.3	0.2613	2.44	48.3	0.1675	1.57	31	0.0347	0.32	6.4
105–110	24.72	0.0473	0.19	5.2	0.402	1.63	44.4	0.3935	1.59	43.4	0.0631	0.26	7
165–175	17.83	0.0005	0.003	0.2	0.0114	0.06	5.4	0.1322	0.74	63	0.0656	0.37	31.3
189–190	10.11	0.0006	0.01	0.5	0.0152	0.15	13.8	0.0742	0.73	67.4	0.0201	0.2	18.3

Table 2. REE concentrations (ppm) in sediments from Site 35 (horizon 20–25 cm)

Element	3.5N H ₂ SO ₄			1M NH ₂ OH · HCl + 25% CH ₃ COOH			Bulk content	X (n = 3)	S _{n-1}	R = S _{n-1} /X, %
	leachate	residue	total	leachate	residue	total				
La	168	7.60	176	168	12.5	181	185	180	5	3
Ce	163	34.8	198	163	35.2	198	208	202	6	3
Pr	47.3	1.52	48.8	46.2	3.17	49.4	49.7	49.3	0.4	1
Nd	199	5.80	205	198	13.0	211	221	212	8	4
Sm	45.9	1.10	47.0	45.9	2.98	48.9	49.2	48	1	2
Eu	11.5	0.30	11.8	11.1	0.86	11.9	12.4	12.0	0.3	3
Gd	44.5	1.10	45.6	47.3	2.83	50.1	54.9	50	5	9
Tb	7.19	0.15	7.34	7.62	0.39	8.01	8.35	7.9	0.5	7
Dy	47.8	0.99	48.8	49.0	2.24	51.3	54.0	51	3	5
Ho	10.2	0.20	10.4	10.4	0.45	10.9	11.2	10.8	0.4	4
Er	29.1	0.55	29.6	30.1	1.25	31.4	31.6	31	1	4
Tm	4.08	0.09	4.17	4.24	0.21	4.45	4.53	4.4	0.2	4
Yb	26.2	0.50	26.7	26.8	1.68	28.5	28.0	27.7	0.9	3
Lu	4.00	0.09	4.09	4.06	0.20	4.26	4.34	4.2	0.1	3

Note: Based on the analysis of three parallel samples by the ICP-MS method. (X) Average of three determinations; (S_{n-1}) standard deviation; (R) relative standard deviation.

1967) and 3.5N H₂SO₄ leachates (Volkov *et al.*, 1979). Weighed samples (10–50 mg) were processed at room temperature and under periodic shaking in 20 ml of the Chester reactive for 4 h or the sulfuric reactive for 2 h. Then the samples were passed through a paper filter (pore size 1–2 μm), the hydroxylamine was decomposed by concentrated HNO₃ under heating, the sulfuric acid was boiled down, and the obtained material was transferred to 5% HNO₃ solution for the subsequent analysis. The filter with residue left after leaching (hereafter, leachate residue) was placed on a platinum dish and incinerated on a gas burner. The sample was subsequently decomposed according to the above-described procedure.

Based on preliminary data, leachate residues are more informative owing to a high concentration of the

labile fraction in sediments from Site 35. The discrepancy between the total (residue + leachate) sum and the bulk sample was generally less than 5% and did not exceed 10% for Gd (Table 2). The present work is primarily based on the study of leachate residues. This method made it possible to avoid the formation of low-soluble sulfates of alkaline earth elements, which are difficult to dissolve in a dilute nitric acid, and the possible precipitation of trace elements together with sulfates during the sulfuric leachate evaporation.

RESULTS

Sediments

Data on the composition of sediments from nine horizons at Site 35 are given in Table 3. The surficial

horizon represents a redeposited carbonate mud (Dubinin, 1998; Dubinin and Volkov, 1992). Clayey sediments are enriched in Fe (6.75–13.2%), Mn (2.24–3.81%), and P (0.526–2.51%) but depleted in Al (4.18–7.37%), relative to the average composition of pelagic clays from the South Basin (Migdisov *et al.*, 1979). These sediments are also depleted in Si and Ti (Dubinin and Volkov, 1992). The Mn/Fe ratio increases from 0.33 at the upper horizon (12–15 cm) to 0.45 at the lower horizon (165–166 cm). These values are higher than the average value (0.22) for pelagic clays from the South Basin (Migdisov *et al.*, 1979). At the lowermost horizon (180–190 cm), the Fe content increases, and the Mn/Fe ratio consequently decreases to 0.27, which is close to the value for metalliferous sediments from the central EPR (Dubinin and Volkov, 1986). High Fe and Mn contents in Site 35 sediments suggest the influence of a hydrothermal source of material. Based on the Boström criterion of hydrothermal endowment in sediments, i.e., the parameter $Al/(Al + Fe + Mn) < 0.4$ (Boström, 1973), sediments above the horizon 60–64 cm are not hydrothermal products (Fig. 1). These sediments are enriched in trace elements (Table 3), and the REE distribution is characterized by a dramatic negative Ce anomaly similar to that in the deep ocean water (Fig. 3). The analysis of clayey sediments from eight horizons revealed a significant positive correlation (probability level, $P = 0.95$) between the following pairs: Fe–(Cu, Eu); P–(Ce, Er, Lu, Mn); Mn–REE (without exception); and Co–(Ce, Mn). Aluminum has a significant negative correlation with REE, Fe, and Mn. These correlations suggest that the lithic source of material served as a diluting agent during the accumulation of Fe, Mn, and REE in sediments. The positive correlation between P, Mn, and REE indicates that these elements were mainly derived from the ocean water.

The form of elements in sediments was studied in the 1M $NH_2OH \cdot HCl + 25\% CH_3COOH$ and 3.5N H_2SO_4 leachates. Based on preliminary results, the REE extraction is commonly close to 100%, and the discrepancy between values simultaneously obtained from the bulk sample and its leachate plus residue is fraction 3–5%; i.e., the discrepancy is at the reproducibility level of the ICP-MS method (Table 2). Therefore, we determined element concentrations not in leachates but in residues left after leaching. The amount of element transferred to leachate was indicated by the difference in contents measured in residue and bulk sample. Table 4 presents data on the distribution of REE, Fe, Mn, Al, and P at different horizons (12–15, 64–65, and 189–190 cm). Note that the REE distribution is given for two additional horizons (20–25, and 160–165 cm).

According to Chester and Hughes (1967), the 1M $NH_2OH \cdot HCl + 25\% CH_3COOH$ leachate can extract manganese oxyhydroxides and poorly crystallized iron oxyhydroxides, and aluminosilicates are only slightly destroyed in the process. In contrast, the 3.5N H_2SO_4 leachate (Volkov *et al.*, 1979) cannot practically extract manganese(IV) oxyhydroxides but can extract more Fe

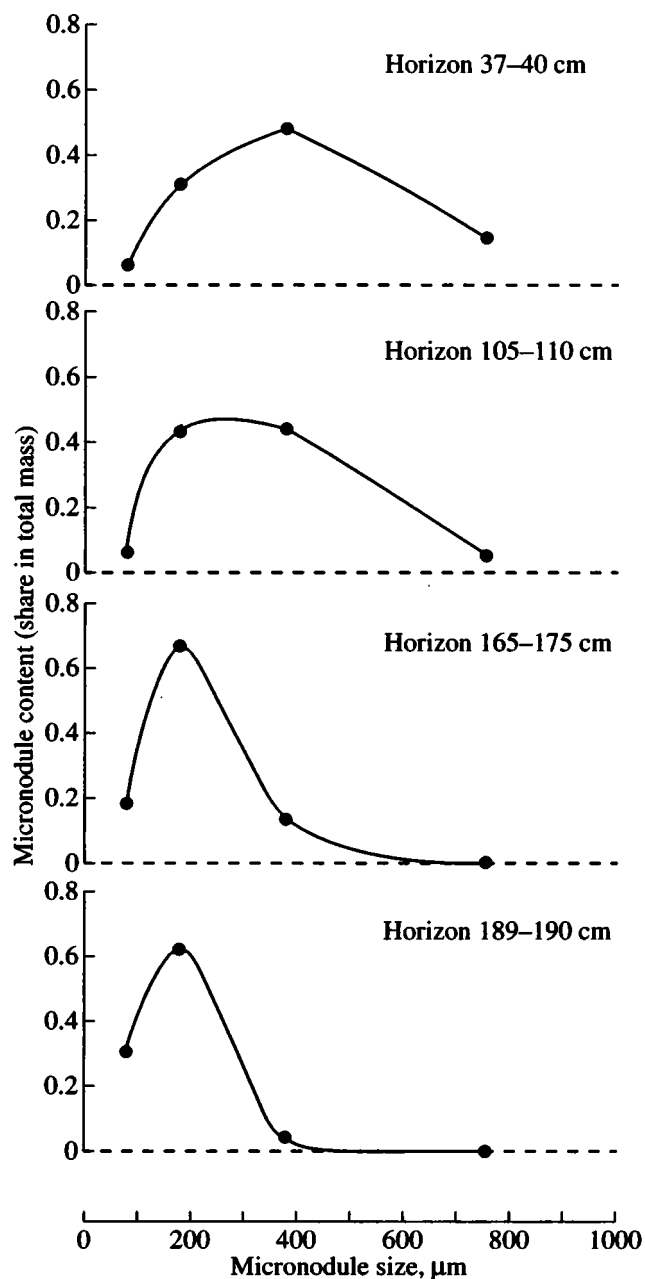


Fig. 2. Ferromanganese micronodule content (share in total mass) vs. fraction size at different horizons. Data points are given at mid-positions of fraction intervals.

from oxyhydroxides and destroy aluminosilicates. Data on the Al content in leachates demonstrate that the sulfuric acid more efficiently decomposes aluminosilicates and extracts two times more Al from clayey sediments (Tables 3, 4). Practically the whole Mn is transferred to the Chester leachate, while the Mn proportion in the sulfuric leachate is less than 13% of its bulk content in samples. The Fe extraction varies from 16.6 to 27.8% of the bulk content, and the difference between the Chester and sulfuric leachates does not exceed 3%.

Table 3. Analytical data on sediments and ferromanganese formations (crust and nodules) at Site 35

Element	Sediments, horizons (cm)									Ferromanganese crust and nodules, depth (cm)				
	0-10	12-15	20-25	60-64	64-68	110-115	160-165	165-166	180-190	crust	0-3	64-68	158-159	165-166
La	13.1	201	185	233	277	308	374	399	411	134	140	98.8	58.3	57.5
Ce	13.5	185	208	251	255	298	337	336	343	767	608	1160	812	580
Pr	3.44	49.6	49.7	62.8	71.2	80.1	94.0	98.7	106	32.8	36.8	26.0	15.0	14.9
Nd	16.6	225	221	275	315	344	418	423	477	137	142	108	64.9	64.1
Sm	3.65	48.7	49.2	60.4	67.8	75.5	93.0	93.5	102	29.4	30.9	24.6	14.5	14.0
Eu	0.85	12.3	12.4	15.5	17.4	18.0	22.7	22.5	26.1	7.34	7.44	6.09	3.69	3.69
Gd	4.40	58.0	54.9	68.4	80.8	91.3	105	109	119	32.9	32.9	26.4	15.3	15.3
Tb	0.59	8.25	8.35	9.80	11.5	13.0	15.1	15.8	17.2	4.89	5.22	3.68	2.27	2.20
Dy	3.94	57.3	54.0	65.6	75.6	86.2	101	108	115	31.3	32.8	23.2	13.9	12.5
Ho	0.81	11.8	11.2	13.2	15.9	17.9	21.2	21.4	23.1	6.08	6.97	4.52	2.73	2.57
Er	2.34	34.1	31.6	38.9	47.4	53.6	62.9	62.9	67.9	17.7	19.4	12.3	7.72	7.28
Tm	0.30	4.92	4.53	5.64	6.76	7.17	8.51	9.00	9.35	2.57	2.77	1.73	1.05	0.98
Yb	1.91	30.8	28.0	35.3	40.3	45.8	51.8	53.0	57.1	16.2	17.3	11.7	6.90	6.26
Lu	0.34	4.62	4.34	5.41	6.58	6.79	7.94	7.85	8.54	2.68	2.67	1.82	1.07	0.98
Fe	0.28	6.75	6.85	7.52	7.83	7.99	8.10	8.39	13.2	11.0	12.7	22.3	23.7	25.4
Mn	0.06	2.24	2.60	2.80	3.08	3.36	3.60	3.81	3.50	12.2	20.6	11.7	12.8	7.70
Al	0.36	7.37	7.33	6.77	6.11	6.09	5.40	5.53	4.18	4.52	2.66	3.03	3.06	3.82
Co	0.011	0.036	0.057	0.060	0.053	0.060	0.065	0.073	0.068	0.249	0.366	0.283	0.208	0.131
Ni	0.013	0.058	0.057	0.045	0.073	0.077	0.092	0.081	0.061	0.319	0.619	0.186	0.285	0.179
Cu	0.003	0.043	0.039	0.038	0.040	0.039	0.039	0.037	0.055	0.210	0.434	0.143	0.179	0.153
P	0.034	0.526	0.940	1.43	1.68	2.22	2.51	1.89	1.71	0.330	0.330	0.543	0.439	0.465
CaCO ₃	95.3	4.6	n.d.	n.d.	n.d.	10.4	2.4	5.0	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
C _{org}	0.11	0.08	n.a.	n.a.	0.06	0.06	0.08	n.a.	0.05	0.03	n.a.	n.a.	n.a.	n.a.
Mn/Fe	0.23	0.33	0.38	0.37	0.39	0.42	0.44	0.45	0.26	1.11	1.61	0.52	0.54	0.30
Ce/Ce*	0.44	0.40	0.47	0.45	0.40	0.41	0.39	0.37	0.36	2.53	1.84	4.98	5.98	4.32

Note: REE concentrations are given in ppm; other elements, in %. (n.d.) not detected; (n.a.) not analyzed; $Ce/Ce^* = 2Ce/Ce^{NASC}/(La/La^{NASC} + Nd/Nd^{NASC})$.

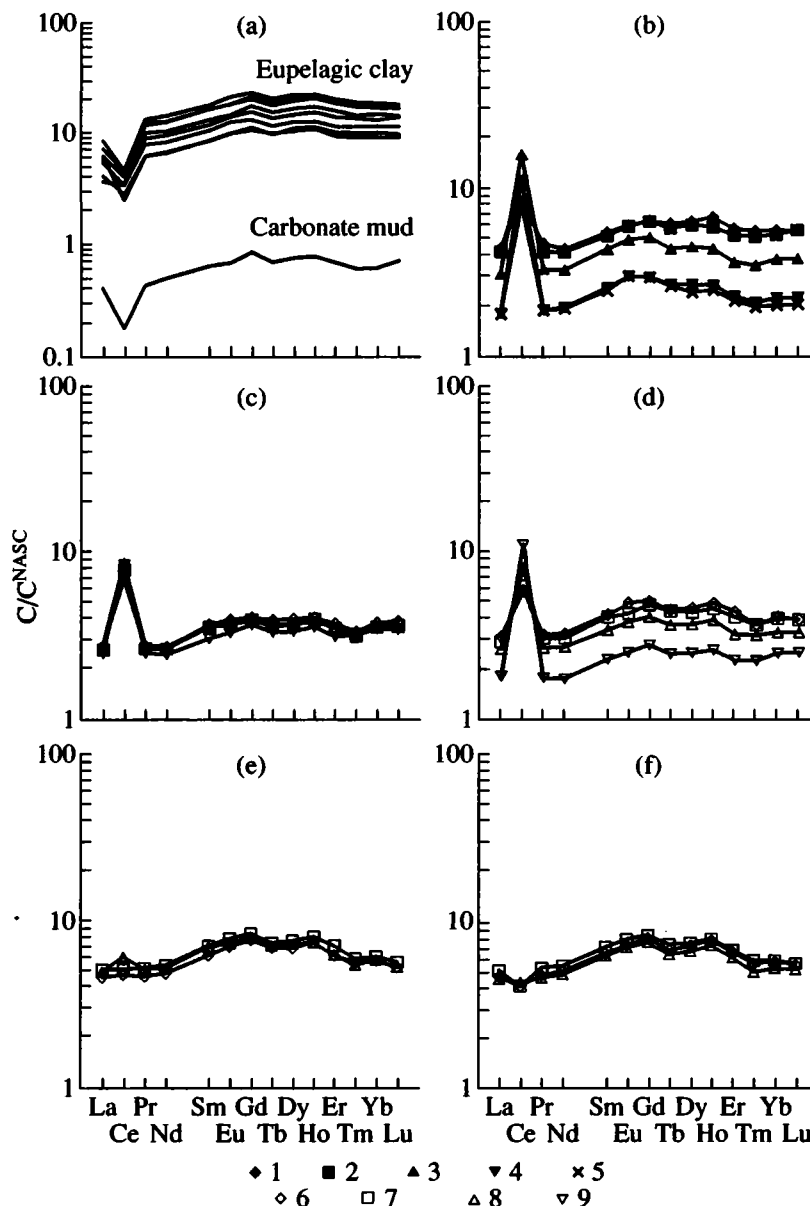


Fig. 3. The NASC-normalized REE distribution (Gromet *et al.*, 1984) in Site 35 sediments. (a) Sediments; (b) ferromanganese nodules and crust; ferromanganese micronodules: (c) horizon 37–40 cm, (d) horizon 105–110 cm, (e) horizon 165–175 cm, (f) horizon 189–190 cm. (1) Ferromanganese nodule (horizon 0–3 cm); (2) ferromanganese crust; (3) ferromanganese nodule (64–68 cm); (4) ferromanganese nodule (158–159 cm); (5) ferromanganese nodule (165–166 cm); ferromanganese micronodules: (6) 50–100 μm , (7) 100–250 μm , (8) 250–500 μm , (9) >500 μm .

Judging from the literature data, the Fe extraction from normal pelagic sediments by two consecutive Chester leachates is less effective, relative to one sulfuric leachate (Volkov *et al.*, 1979). The sulfuric leachate can extract up to 100% Fe represented by amorphous and poorly crystallized oxyhydroxides from metalliferous sediments in the central EPR (Dubinin and Volkov, 1992). According to Migdisov *et al.* (1979), the efficiency of Fe extraction from metalliferous sediments by the Chester reactive is only 52% of the total Fe content. During the processing of sediments from Site 35,

both leachates practically extract a similar amount of Fe but significantly different amounts of Al. In other words, the Fe transfer to leachates does not depend on the amount of destroyed aluminosilicates. Hence, the oxyhydroxide modification rather than the aluminosilicate modification of Fe prevails in sediments from Site 35.

It is worth noting that the Mn transfer to leachate is not governed by the amount of extracted Fe. During a simultaneous application of the 1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 25% CH_3COOH and 3.5N H_2SO_4 leachates for processing the ferromanganese crust, in which Fe is par-

Table 4. Analytical data on residues of Site 35 sediments left after the treatment with (1) 3.5N H₂SO₄ and (2) 1M NH₂OH · HCl + 25% CH₃COOH

Element	Horizon, cm									
	12–15		20–25		64–68		160–165		180–190	
	1	2	1	2	1	2	1	2	1	2
La	9.15	12.7	7.60	12.5	9.32	14.3	11.2	28.1	11.0	19.1
Ce	33.0	34.5	34.8	35.2	36.0	28.4	47.0	38.4	54.1	28.4
Pr	1.43	2.86	1.52	3.17	1.91	3.77	2.69	6.95	2.51	5.22
Nd	5.48	12.0	5.80	13.0	7.16	16.1	10.5	27.9	10.8	23.0
Sm	0.97	2.62	1.10	2.98	1.39	3.31	2.02	6.49	1.88	5.33
Eu	0.34	0.78	0.30	0.86	0.35	0.93	0.55	1.58	0.48	1.49
Gd	1.02	2.68	1.10	2.83	1.53	3.76	2.35	6.77	2.29	5.95
Tb	0.14	0.42	0.15	0.39	0.22	0.49	0.28	0.93	0.36	0.90
Dy	0.97	2.50	0.99	2.24	1.40	3.41	1.60	5.52	2.05	5.57
Ho	0.17	0.54	0.20	0.45	0.28	0.76	0.35	1.19	0.37	1.14
Er	0.46	1.55	0.55	1.25	0.84	2.25	1.02	3.43	1.30	3.64
Tm	0.07	0.26	0.09	0.21	0.10	0.30	0.15	0.49	0.20	0.47
Yb	0.52	1.38	0.50	1.68	0.79	1.82	1.15	3.47	1.37	3.31
Lu	0.06	0.21	0.09	0.20	0.12	0.32	0.15	0.45	0.19	0.45
P	0.024	0.067	–	–	0.042	0.117	–	–	0.129	0.334
Fe	4.97	5.07	–	–	5.65	5.78	–	–	11.0	10.6
Mn	2.00	0.03	–	–	2.67	0.03	–	–	3.15	0.04
Al	4.13	6.12	–	–	3.63	5.21	–	–	3.35	3.63
Ni	0.045	<0.001	–	–	0.048	0.010	–	–	0.057	0.019
Co	0.035	0.009	–	–	0.044	0.003	–	–	0.048	0.008
Cu	0.024	0.018	–	–	0.028	0.018	–	–	0.043	0.037
Mn/Fe	0.40	0.00	–	–	0.47	0.00	–	–	0.29	0.00
Ce/Ce*	1.93	1.25	2.21	1.22	1.85	0.84	1.87	0.60	2.24	0.62

Note: REE concentrations are given in ppm; other elements, in %. Contents of P, Fe, Al, Mn, Ni, Co, and Cu were not determined in residues from horizons 20–25 and 160–165 cm.

tially included in vernadite, the Chester leachate extracted 60% Fe, while the sulfuric leachate extracted only about 37% Fe (Dubinin, 1998). Hence, the correlation between oxyhydroxides of Fe and Mn is very weak.

Phosphorus is more effectively extracted by the sulfuric leachate (up to 98%), relative to the Chester leachate (80–92%). Phosphorus can occur in absorbed form, bone detritus, or organic matter in sediments. First two forms prevail in pelagic sediments. Phosphorus is included in the secondary apatite and iron oxyhydroxides (as phosphate ion) in ferromanganese sediments of the ocean. It can also be present in hydroxophosphates, if ferromanganese oxyhydroxide aggregates are lacking (Dubinin *et al.*, 1997). Although iron and manganese hydroxides have similar sorption capacities, iron oxyhydroxide can absorb ten times more P than the manganese dioxide (Balistrieri and Chao, 1990). Contents of P and Fe are directly corre-

lated in leachates (Fig. 4). Hence, phosphorus is associated with iron oxyhydroxides and likely to be included in hydroxophosphate in sediments from Site 35. In sediments from Site 35, the >50- μ m-fraction zeolite contains ferrocalsium hydroxophosphate with the formula Ca₂FePO₄(OH)₄ (Dubinin and Sval'nov, 1997).

Regardless of the leachate type, as much as 88 to 98% REE(III) is transferred to the solution (Tables 3, 4). The high REE yield in leachates suggests that rare earth elements primarily occur in the studied samples as absorbed elements (Dubinin, 1998). The REE signature in the labile fraction mimics the pattern in bulk samples characterized by a negative Ce anomaly at all horizons. The REE signature in leachate residues is more informative. Since practically the whole Mn is transferred to solution after the Chester reactive treatment, the remaining REE portion characterizes the geochemistry of iron oxyhydroxides (hydroxophosphates). Like Fe and P, the three-valent REE species are always more

concentrated in the Chester leachate residue, testifying to a stronger correlation of REE(III) with iron oxyhydroxides (hydroxophosphates). The Ce anomaly in the REE signature of the Chester leachate residue indicates that hydrothermal iron hydroxophosphate is present in sediments and the anomaly is directly correlated with the $Al/(Al + Fe + Mn)$ value in bulk samples (Table 4; Figs. 1, 5). However, the Ce behavior differs from that of other rare earth elements. The Ce excess, relative to REE(III), is directly related to the Mn abundance in sediments (Table 4; Fig. 5) in residues of the sulfuric acid leachate. In addition to aluminosilicates, well-crystallized ferromanganese oxyhydroxides are left in the residue of sulfuric leachates. The Ce excess is an evidence of the correlation between Ce and Mn as a result of their oxidation in surficial waters (Moffett, 1990).

The dissolution of Mn in the Chester leachate prompts the Co and Ni transfer to the solution, confirming the correlation data on sediments (Table 4).

Ferromanganese Micronodules

The chemical composition of micronodules from four horizons is presented in Table 5. Contents of Fe and Mn in different fractions from one horizon are characterized by an insignificant variation. The Fe content increases from fine to coarse fractions only at horizon 165–175 cm. The Mn content increases in coarser fractions from horizon 105–110 cm. The Al distribution is similar in both micronodules and sediments. Since the Al content increases from 4.18% at horizon 180–190 cm to 7.37% at horizon 12–15 cm, the Al content in finest fractions also increases from 2.6–2.8% at the lowermost horizon to 3.4% at the intermediate horizon and 3.5% at the uppermost horizon (Fig. 6). Variations in Fe (Fig. 6) and P are also reflected in the micronodule composition. The Mn/Fe ratio is minimal at horizon 189–190 cm (0.7–0.8) and increases to 1.6 in the >500- μ m-fraction at horizon 105–110 cm. In coarser micronodule fractions, the Mn/Fe ratio generally decreases at horizons 165–175 and 189–190 cm but increases at horizons 37–40 and 105–110 cm (Fig. 7).

The trace element distribution in micronodules from four horizons at Site 35 is presented in Table 5, while the NASC-normalized REE distribution is shown in Fig. 3. The distribution of REE (excluding Ce) in separate micronodule fractions is similar, except for horizon 105–110 cm. The REE(III) distribution shows a maximum in the IREE region. Based on the correlation analysis of 14 micronodule samples, the REE(III) distribution is a function of the P content. The Ce distribution appreciably differs from that of other rare earth elements. Elsewhere (except horizon 37–40 cm, fraction >500 μ m), the Ce concentration increases in coarser fractions and at upper horizons. The Th distribution is also similar at horizons 37–40 and 105–110 cm, testifying to a strong correlation between Ce and Th ($r = 0.957$). Based on the available data, REE(III) correlate

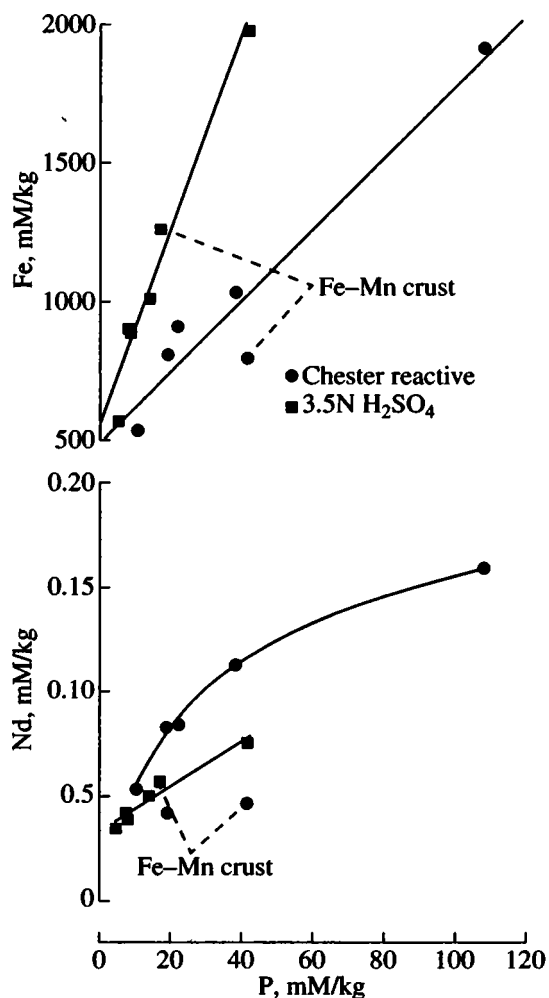


Fig. 4. The Fe and Nd vs. P plot for residues left after the leaching of eupelagic clays and ferromanganese crusts (Dubinin, 1998).

with P and Fe as well ($r = 0.765$ – 0.819). Ce, Th, Mo, W, and Co correlate with Mn.

In order to assess the lithic material content in micronodule nuclei, we collected loose micronodule samples (weight ≤ 50 mg; three fractions from horizon 37–40 cm and two fractions from horizon 189–190 cm) that were treated in 20 ml of the Chester reactive for 4 h. These samples were simultaneously taken from sediments and should not be confused with the samples presented in Tables 1 and 5. The filtrate and leachate residue were separately analyzed (Table 6). The obtained results differ little from data on separate fractions from a single horizon. However, micronodules from different horizons are characterized by some specific features. The Fe signature in leachates is most contrasting. For example, the labile Fe content in three studied fractions is, on the average, 65% of total Fe at horizon 37–40 cm but only 37% at horizon 189–190 cm. This decrease is caused by the crystallization of iron oxyhydroxides in older sediments (Volkov *et al.*, 1979).

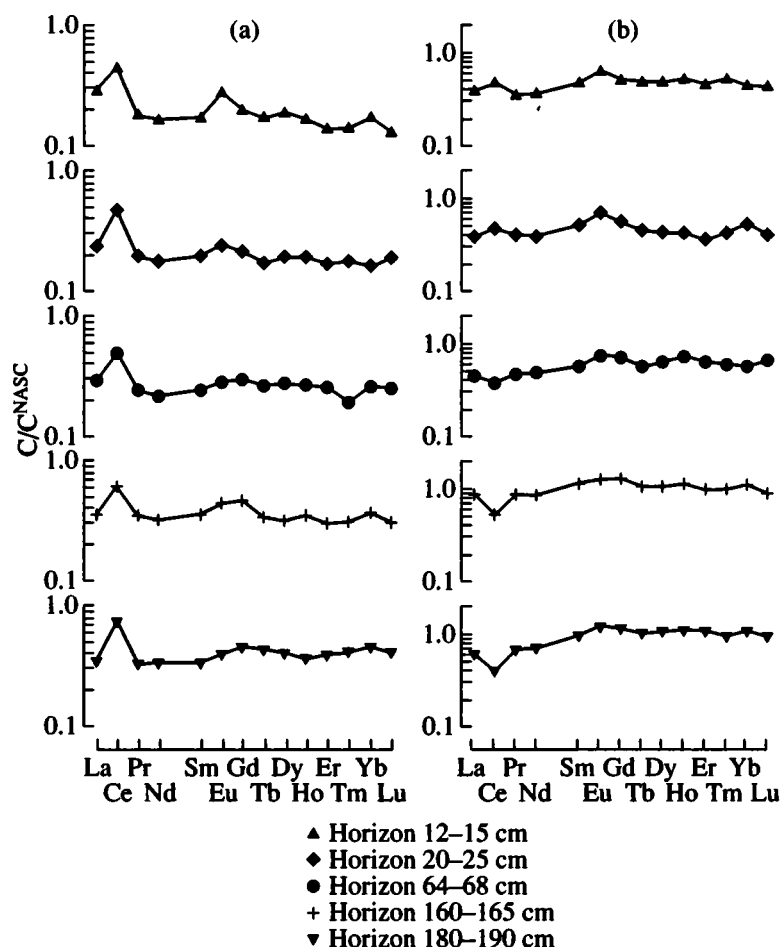


Fig. 5. The NASC-normalized REE distribution (Gromet *et al.*, 1984) in residues of Site 35 sediments after the treatment with (a) 3.5N H_2SO_4 and (b) 1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 25% CH_3COOH .

The strong correlation between P and Fe was probably responsible for the low scale of phosphorus transfer to the leachate. Our data on the processing of bottom sediments with the Chester reactive revealed that phosphorus in bone detritus is completely transferred to the leachate (Dubinin and Strekopytov, 1994). Only phosphorus associated with iron oxyhydroxides can remain in the residue. As much as 51–54% and 71–76% of the total P is transferred to leachates at horizons 37–40 and 189–190 cm, respectively. This observation also testifies to the higher degree of iron oxyhydroxide crystallization at older horizons, since admixtures are removed from mineral structure during the crystallization. Some elements, such as Mn, Ni, and Co, are completely transferred to the leachate. The Al yield is equal to 22% at horizon 37–40 cm and 33% at horizon 189–190 cm. The REE yield varies from 88–92% at horizon 37–40 cm to as much as 94–97% at horizon 189–190 cm. The high REE yield in leachates indicates a weak connection of rare earth elements with the aluminosilicate portion of micronodule nuclei. These elements are pri-

marily connected with ferromanganese oxyhydroxides in the ore shell.

Macronodules and Ferromanganese Crust

In addition to micronodules, macronodules and crust (detected under the carbonate mud layer at a depth of 10 cm at Site 35) were also studied (Dubinin, 1998). Among four nodules discovered here, three nodules represent the buried variety. Compositions of nodules and crust are presented in Table 3. As a result of the high Fe content, the buried nodules are characterized by a low Mn/Fe ratio (0.3–0.5). In contrast, the surficial nodule and crust have an appreciably higher Mn/Fe value (1.1–1.6). The Mn/Fe and total (Co + Ni + Cu) values in studied nodules are shown in Fig. 8. Compositions of micronodules are also presented in the same figure for comparison. Most micronodules (horizons 37–40, 105–110, and 165–175 cm), along with the surficial nodule (horizon 0–3 cm) and ferromanganese crust, fall into the domain of hydrogenic formations. Deep-seated micronodules (189–190 cm) with a higher

Table 5. Analytical data on micronodules from Site 35

Element	Horizon 37–40 cm				Horizon 105–110 cm				Horizon 165–175 cm			Horizon 189–190 cm		
	50–100 μm	100–250 μm	250–500 μm	>500 μm	50–100 μm	100–250 μm	250–500 μm	>500 μm	50–100 μm	100–250 μm	250–500 μm	50–100 μm	100–250 μm	250–500 μm
La	87.9	83.5	88.7	79.3	101	93.6	84.6	58.5	147	165	159	153	168	147
Ce	500	571	629	611	425	456	585	802	347	374	450	305	306	324
Pr	21.6	21.0	21.9	19.7	25.3	24.2	21.1	14.0	36.7	41.6	40.7	38.8	43.1	37.2
Nd	89.5	87.3	90.4	80.7	108	102	89.8	57.8	160	181	173	171	185	163
Sm	21.1	20.4	20.6	17.4	24.2	23.3	19.6	13.1	35.8	40.9	40.2	38.0	41.4	36.7
Eu	4.90	4.57	4.68	4.13	6.10	5.28	4.72	3.14	8.81	9.87	9.23	9.21	10.0	8.99
Gd	21.1	20.5	20.5	19.1	26.2	25.0	21.2	14.6	40.5	44.3	41.8	42.7	44.6	40.2
Tb	3.35	3.08	3.18	2.84	3.79	3.73	3.12	2.11	5.96	6.38	6.11	5.92	6.43	5.61
Dy	20.9	19.1	19.4	17.5	23.9	22.5	19.1	13.1	36.3	40.3	38.5	38.7	40.1	35.7
Ho	4.23	4.16	4.03	3.73	5.10	4.72	4.05	2.71	7.86	8.54	7.84	8.30	8.49	7.72
Er	12.8	12.1	12.0	10.7	14.9	13.8	11.0	7.74	21.5	24.6	21.6	23.2	23.9	21.4
Tm	1.68	1.58	1.61	1.61	1.83	1.84	1.60	1.13	2.87	3.02	2.77	2.89	3.04	2.58
Yb	11.8	11.2	11.0	10.8	12.6	12.4	10.3	7.78	18.3	19.3	18.4	18.6	18.8	16.8
Lu	1.87	1.76	1.72	1.67	1.89	1.89	1.60	1.22	2.58	2.78	2.58	2.76	2.80	2.57
Th	8.00	10.1	12.8	13.8	7.88	8.47	11.1	16.3	6.90	7.39	6.90	6.43	5.28	4.72
Mo	341	375	375	299	541	550	613	674	409	402	389	410	401	370
W	40	46	44	42	54	58	64	77	35	34	35	45	32	31
Fe	12.8	13.0	12.4	10.6	13.8	13.3	12.5	13.0	13.9	15.1	17.1	19.5	19.5	20.0
Mn	14.2	16.2	17.7	14.2	15.1	17.4	18.9	20.6	17.1	16.1	16.9	14.9	15.5	14.5
Al	3.54	3.80	3.76	4.45	3.37	3.18	2.72	2.12	2.71	2.77	2.72	2.63	2.84	2.41
Ti	0.73	0.53	0.57	0.55	0.98	0.49	0.48	0.57	0.29	0.22	0.33	<0.03	<0.03	<0.03
Co	0.29	0.34	0.41	0.34	0.34	0.42	0.48	0.59	0.31	0.30	0.28	0.24	0.22	0.16
Ni	0.48	0.46	0.45	0.36	0.42	0.48	0.49	0.47	0.64	0.55	0.53	0.41	0.49	0.55
Cu	0.23	0.15	0.18	0.16	0.16	0.13	0.15	0.16	0.15	0.13	0.14	0.13	0.13	0.14
P	0.499	0.484	0.460	0.477	0.728	0.626	0.602	0.500	1.04	1.09	0.996	1.11	1.16	0.986
Ca	2.60	2.53	2.41	2.34	3.65	2.68	2.70	2.61	3.40	3.07	3.51	4.04	3.38	3.74
Mn/Fe	1.11	1.25	1.43	1.34	1.10	1.31	1.51	1.58	1.22	1.07	0.99	0.76	0.80	0.73
Ce/Ce*	2.51	2.98	3.13	3.40	1.81	2.08	2.99	6.14	1.01	0.96	1.21	0.84	0.77	0.93

Note: Concentrations of REE, Th, Mo, and W are given in ppm; other elements, in %.

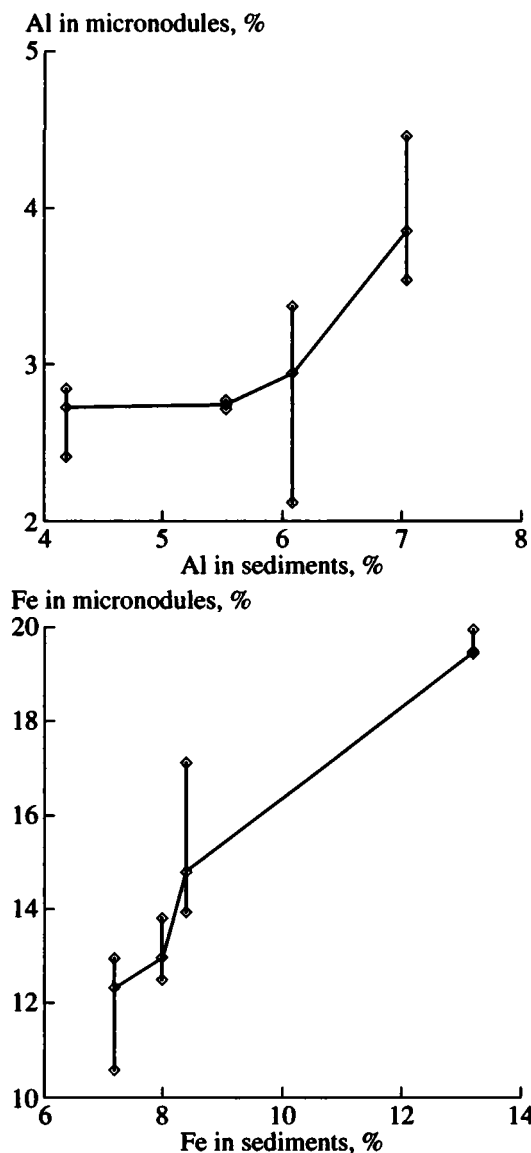


Fig. 6. The Fe and Al distribution in micronodules (weighted mean contents) vs. host sediments (average contents). Minimal and maximal values of element contents are given for each horizon.

Fe content and all buried nodules fall into the domain of metalliferous (hydrothermal) sediments. The $(\text{Co} + \text{Ni} + \text{Cu})/\text{Mn}$ ratio in all oxyhydroxides is close to 0.060 ± 0.005 .

The REE distribution in nodules and crust is characterized by a positive Ce anomaly (Fig. 3), while buried nodules are enriched in IREE. The REE(III) concentrations in the surficial nodule, ferromanganese crust, and buried nodules (horizons 158–159 and 165–166 cm) are similar lower, relative to those in host clays. In micronodules and three buried nodules, only the P-REE(III) correlation ($r = 0.93\text{--}0.97$, $n = 17$) remains valid, the Fe-REE correlation is insignificant ($P = 0.95$,

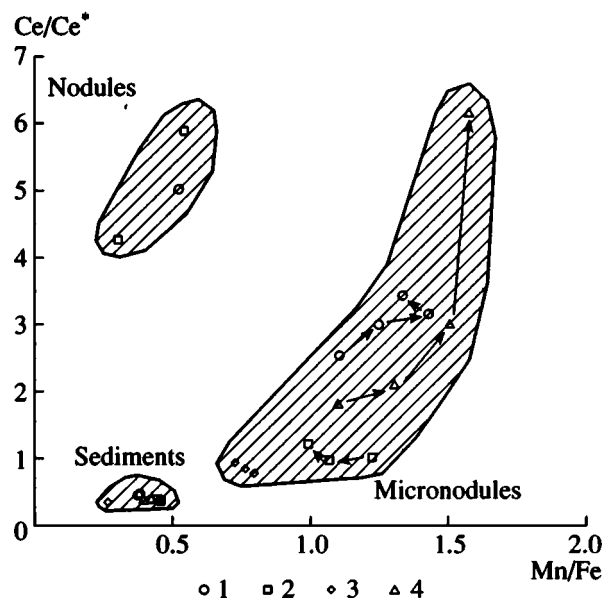


Fig. 7. The Ce anomaly $\text{Ce}/\text{Ce}^* = 2 \times \text{Ce}/\text{Ce}^{\text{NASC}}/(\text{La}/\text{La}^{\text{NASC}} + \text{Nd}/\text{Nd}^{\text{NASC}})$ vs. Mn/Fe in ferromanganese micronodules. Horizons: (1) 37–40 cm, (2) 105–110 cm, (3) 165–175 cm, (4) 189–190 cm. Arrows indicate compositional changes in micronodules from the fine to coarse fraction. Domains of host sediments, micronodules, and buried ferromanganese nodules are hatched.

$r < 0.482$, $n = 17$). The correlation of Al with REE and P is inverse, while Mn has a positive correlation with Ni ($r = 0.74$) and Co ($r = 0.80$). Thus, we observe stable P-REE (except Ce) and Mn-(Ni, Co) correlations in micronodules and buried nodules. It is worth noting that the P-REE(III) correlation is marked by a regression value close to zero at the intercept with the Y axis, suggesting that the endowment of other REE-carriers, in addition to phosphates, is negligible (Fig. 9).

DISCUSSION

Sediments

The decrease in hydrothermal material input into sediments at Site 35 resulted in a gradual depletion in Fe and Mn that are major constituents of the hydrothermal material. Nevertheless, at horizon 12–15 cm, the Mn content exceeds the average value for pelagic clays from the South Basin (Migdisov *et al.*, 1979). Higher REE concentrations registered here are primarily related to the delivery of hydrothermal ferromanganese oxyhydroxides, as evidenced by an increase in REE, Fe, and Mn downward the core. Metalliferous sediments from the central zone of mid-oceanic ridges are not characterized by so high REE concentrations (Bender *et al.*, 1971; Dubinin and Volkov, 1986; Migdisov *et al.*, 1979; Piper and Graef, 1974). The REE accumulation in metalliferous sediments is caused by the absorption of rare earth elements from deep waters on suspended particulates of the hydrothermal iron

Table 6. Analytical data on (1) leachates and (2) residues of micronodules in Site 35 sediments left after the treatment with 1M $\text{NH}_2\text{OH} \cdot \text{HCl} + 25\% \text{CH}_3\text{COOH}$

Element	Horizon, cm									
	37–40						189–190			
	Fraction, μm									
	50–250		250–500		> 500		50–250		250–500	
	1	2	1	2	1	2	1	2	1	2
La	96.5	10.5	102	9.93	90.8	13.6	176	6.62	169	2.72
Ce	481	61.6	502	55.6	555	69.5	328	23.0	348	16.8
Pr	21.8	2.31	23.3	2.29	16.2	3.15	43.1	1.70	41.0	0.74
Nd	91.8	9.15	96.8	9.07	84.2	12.4	192	7.90	178	3.23
Sm	19.8	2.14	21.0	1.86	18.4	2.67	39.4	1.68	38.0	0.64
Eu	5.07	0.52	4.98	0.49	4.40	0.73	9.80	0.42	8.97	0.21
Gd	24.1	2.18	24.6	2.18	22.0	3.17	46.4	1.76	44.0	0.67
Tb	3.24	0.31	3.38	0.32	2.94	0.44	6.46	0.26	6.15	0.13
Dy	23.7	1.93	23.5	1.99	21.3	2.83	41.3	1.58	37.1	0.75
Ho	4.99	0.39	5.00	0.40	4.35	0.59	8.39	0.38	7.49	0.15
Er	15.5	1.18	15.0	1.08	13.9	1.72	23.1	0.89	22.0	0.41
Tm	2.28	0.16	2.14	0.16	2.10	0.24	3.18	0.14	2.93	0.08
Yb	14.9	1.16	14.1	1.10	13.9	1.57	19.0	1.06	17.1	0.53
Lu	2.34	0.16	2.34	0.17	2.13	0.25	2.83	0.18	2.64	0.08
P	0.203	0.177	0.200	0.170	0.184	0.176	0.900	0.282	0.626	0.262
Fe	7.72	4.28	7.52	3.77	7.07	4.11	7.42	13.1	7.86	12.5
Mn	14.8	0.06	14.8	0.08	14.2	0.09	15.3	0.06	14.6	0.04
Al	0.97	3.51	1.12	3.36	0.86	3.72	0.91	2.18	1.15	1.99
Ni	0.40	<0.01	0.41	<0.01	0.36	<0.01	0.53	<0.01	0.58	<0.01
Co	0.30	<0.01	0.29	<0.01	0.31	<0.01	0.19	0.01	0.18	<0.01
Cu	0.14	<0.01	0.15	<0.01	0.15	<0.01	0.09	0.06	0.09	0.07
Mn/Fe	1.92	0.01	1.96	0.02	2.00	0.02	2.06	0.005	1.86	0.003
Ce/Ce*	2.27	2.79	2.25	2.60	2.82	2.37	0.79	1.42	0.89	2.52

Note: (1) Leachate; (2) residue. REE concentrations are given in ppm; other elements, in %.

oxyhydroxide. The REE accumulation scale depends on the distance from the hydrothermal source (Dubinin and Volkov, 1988; Ruhlin and Owen, 1986). Similar sediments were detected in the Bauer Deep to the east of the East Pacific Rise and within the South Basin to the west of the EPR (Dubinin and Volkov, 1986, 1992; Stoffers *et al.*, 1984b). These sediments are accumulated under conditions of low sedimentation rates away from hydrothermal sources (Dymond *et al.*, 1976).

The Mn enrichment downward the core in eupelagic clays is terminated at horizon 180–190 cm, where one can register a drastic increase in Fe (13.2%). The P distribution is akin to the Mn pattern, and its increase downward the core gives way to an abrupt decrease at horizon 165–166 cm. The P accumulation in metalliferous sediments is caused by the absorption of this ele-

ment from the ocean water on suspended particulates of the hydrothermal iron oxyhydroxide (Feely *et al.*, 1996). Therefore, P and Fe are well correlated (Berner, 1973). The transition from Fe-rich sediments at horizon 180–190 cm to Fe-poor varieties at horizon 165–166 cm is possibly linked to a decrease in the hydrothermal material supply and sedimentation rate. This circumstance is likely to be responsible for the appearance of nodules at horizon 165–166 cm. The drastic compositional change in sediments between horizons 165–166 and 180–190 cm could be induced by the termination of hydrothermal material supply from a local source.

Based on phase analysis data (Table 4), rare earth elements in sediments are associated with P absorbed on iron oxyhydroxides (Fig. 4). Both leachates more

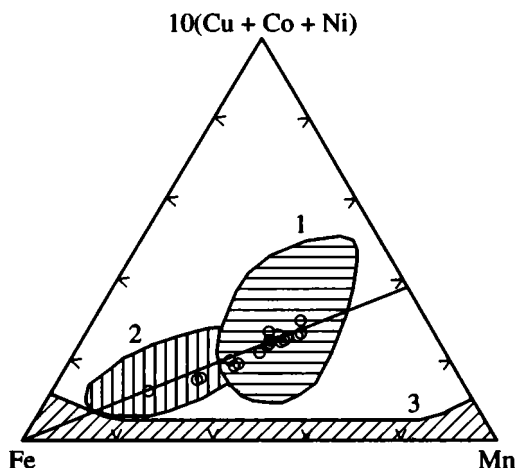


Fig. 8. Compositions of ferromanganese nodules and micronodules from Site 35 on the Fe–Mn–10(Cu + Co + Ni) plot. (1) Domain of deep-water pelagic ferromanganese nodules and crusts; (2) domain of metalliferous sediments and diagenetic nodules from the pelagic margin; (3) domain of hydrothermal ferromanganese sediments and shallow-water diagenetic nodules in rivers and lakes (Bonatti *et al.*, 1972; Volkov and Dubinin, 1987). The straight line across domains 1 and 2 fits the value $(\text{Cu} + \text{Co} + \text{Ni})/\text{Mn} = 0.060 \pm 0.005$.

readily dissolve bone detritus, relative to crystallized iron oxyhydroxides that hamper the mobilization of P and REE. At upper horizons (12–15 and 20–25 cm), sediment residues left after the Chester reactive treatment demonstrate the NASC-type REE distribution with a minor positive Ce anomaly (Table 4; Fig. 5). This kind of REE distribution in iron oxyhydroxides supports the absence of hydrothermal iron oxyhydroxides in sediments. The decrease in the $\text{Al}/(\text{Al} + \text{Fe} + \text{Mn})$ value downward the core is complemented with the appearance of negative Ce anomaly and the LREE depletion in leachate residues (Fig. 1), suggesting the presence of hydrothermal iron oxyhydroxides.

The manganese, primarily Mn(II), extraction by the treatment of sediments with the 3.5N H_2SO_4 solution can reach 13%. The Mn presence is responsible for the positive Ce anomaly in the REE signature of sediments (Fig. 5), and the anomaly magnitude correlates with the Mn content (Table 4). In surficial waters, Ce can enter the manganese oxyhydroxide structure as a result of the oxidation of Mn^{2+} and Ce^{3+} on the surface of suspended particulates (Moffett, 1990; Sholkovitz *et al.*, 1994).

Formation of Ferromanganese Micro- and Macronodules in Sediments

Ferromanganese micro- and macronodules were formed in different sedimentation conditions. It is pertinent to note that micronodule and host sediment compositions are interrelated, as suggested by the comparison of Fe and Al distribution in sediments versus weighted mean values of these elements in micronod-

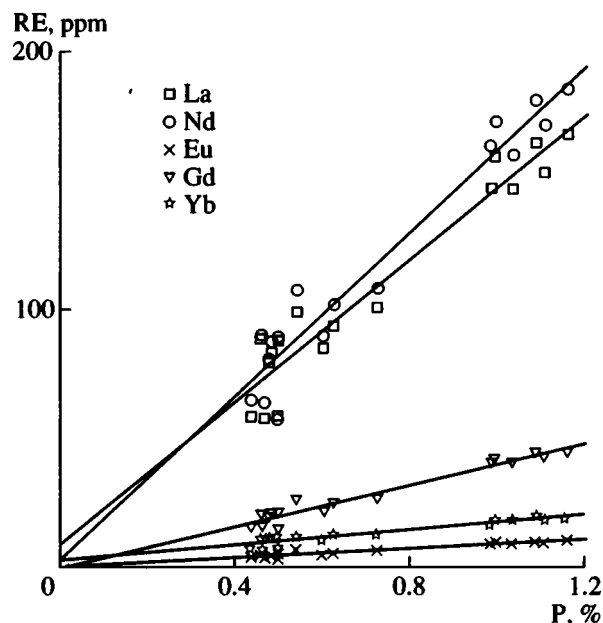


Fig. 9. The REE(III)–P plot for ferromanganese micronodules and buried nodules.

ules (Fig. 6). For example, the comparison of micronodules from horizons 37–40, 105–110, 165–175, and 189–190 cm with sediments from 20–25 (and 60–64), 110–115, 165–166, and 180–190 cm, respectively, well illustrates the above statement. Evidently, the increase in Al in sediments upward the core directly correlates with the Al content in micronodules. This phenomenon is related to the following process: a portion of Al enters micronodules together with iron oxyhydroxides, while another portion is associated with zeolite aggregates in micronodule nuclei. The latter inference is obvious from the data on >500- μm -fraction micronodules characterized by decrease in Fe and Mn but increase in Al, relative to other fractions at horizon 37–40 cm (Table 5). The Ce, Co, Th, and W concentrations, adjusted to ore material contents, reveal that the >500- μm -fraction micronodules are practically indiscernible from counterparts in other fractions from this horizon (Fig. 10). The Fe content in sediments directly correlates with its weighted mean content in micronodules (Fig. 6). An analogous but less prominent pattern is typical of Fe in buried micronodules as well (Table 3). Hence, micronodules rather than nodules are compositionally closer to host sediments. Micronodules and buried nodules also demonstrate similar chemical variations. The REE (III) concentration in micronodules and buried macronodules is governed by P contents (Fig. 9). The Fe–REE(III) correlation is only registered for micronodules. Hence, REE(III) are absorbed on iron oxyhydroxides with phosphate anions (iron hydroxophosphates).

In contrast to other rare earth elements, Ce is associated with the Mn group elements (Ce, Th, Co, Mo, and W). According to (Moffett, 1990; Moffett and Ho, 1996), the association of Ce and Co with Mn is caused by a common mechanism of their oxidation in surficial ocean water. Therefore, the growth of Ce and Co concentrations in the ferromanganese oxyhydroxide suggests the involvement of a hydrogenic source (suspension particulates formed in surficial waters). Thorium is accumulated on suspended particulates throughout the entire water column (Roy-Barman *et al.*, 1996). Micronodules manifest a functional correlation between Ce and Th ($r = 0.957$, $n = 14$), suggesting that these elements have highly similar properties in the four-valent state. The Co, Ce, Th, and W concentrations depend on the fraction size, and their maximal concentration is registered in coarse micronodule fractions from horizons 37–40 and 105–110 cm (Fig. 10). Relative to counterparts from deeper horizons, sediments from these horizons are depleted in hydrothermal material. This phenomenon is likely to be caused by the preferential introduction of hydrogenic material during the micronodule growth.

If micronodules simultaneously originate in a surficial sediment microlayer and then successively grow, we can assume that the coarser micronodule composition reflects the mixture of newly formed and older (finer) fractions. Suppose that micronodules represent spheres with an average diameter equal to the half interval between minimal sizes of adjacent fractions (or their maximal sizes, as suggested by the negligible discrepancy), then we can calculate the element concentration in each discrete interval of fraction size. The calculations were based on a mix model for the middle horizon (105–110 cm) micronodules that were most contrasting in the composition of separate fractions. The correlation of Ce with micronodule dimension (Table 5) is demonstrated by the fact that the oxyhydroxide mass growth in micronodules from this horizon is accompanied by a successive enrichment in Ce (459, 600, and 833 ppm). The Ce concentration in the ferromanganese micronodule from horizon 64–68 cm is equal to 1160 ppm (Table 3), which can be considered the upper limit for sedimentation conditions in the study region. The concentration of hydrogenic elements (Ce, Th, Co, and possibly W) in ferromanganese oxyhydroxides can be caused by the preferential accumulation of hydrogenic material in coarser micronodule fractions.

The Th, Co, and W depletion in larger micronodules at horizons 165–175 and 189–190 cm can also be attributed to the aforesaid process. In lower sections of the core, sediments are enriched in hydrothermal ferromanganese oxyhydroxides that are depleted in hydrogenic elements, except for the low-variable or slightly increasing Ce (Fig. 10). This phenomenon can be explained by results of the phase analysis of sediments (Fig. 5). Coupled with REE(III), Ce makes up a sorptional complex with iron hydroxophosphates in the res-

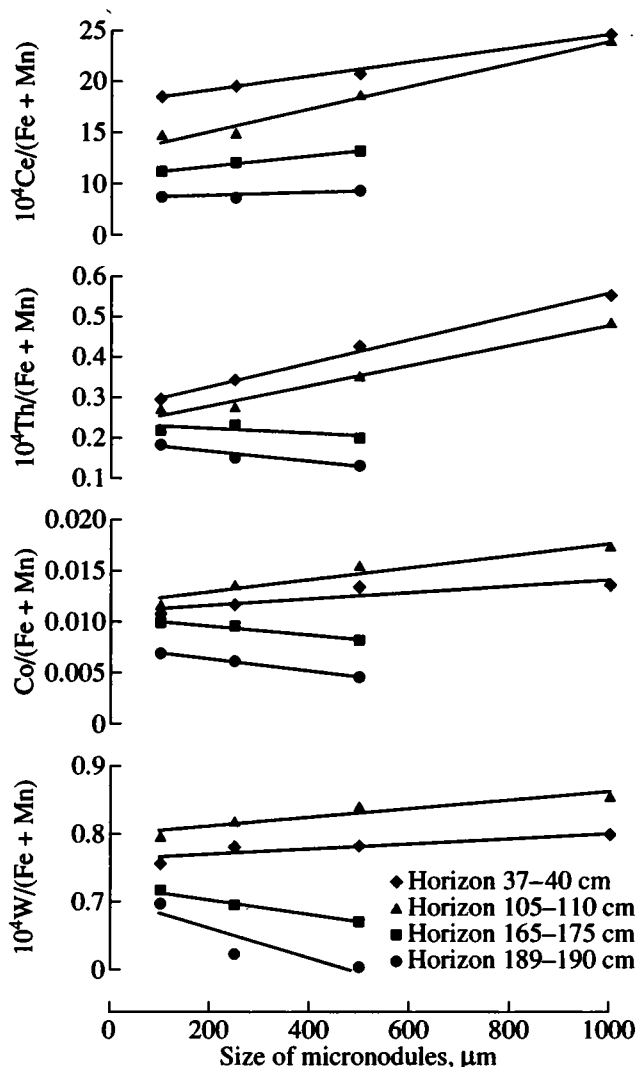


Fig. 10. The (Fe + Mn)-normalized Ce, Th, Co, and W contents vs. maximal size of micronodule fraction.

idue left after the Chester reactive treatment, on the one hand, and enters the hydrogenic component of manganese oxyhydroxides in the residue left after the sulfuric acid treatment, on the other hand.

As mentioned above, micronodules and buried nodules reveal several common compositional features. The REE(III) distribution in nodules and micronodules is governed by the P abundance. The Ce concentration directly correlates with the micronodule dimension and reaches the maximum in macronodules. In micronodules, nodules (horizon 0–3 cm), and ferromanganese crust, the $(\text{Co} + \text{Ni} + \text{Cu})/\text{Mn}$ ratio is 0.060 ± 0.005 . Hence, the compositional signature of macronodules is closely linked to the development of micronodules.

The relationship between different fractions and the compositional instability of micronodules within a single horizon can elucidate the mechanism of micronodule growth. The inheritance of some compositional fea-

tures of host sediments by micronodules (e.g., Fe, and Al, and P distribution) testifies to the involvement of labile fraction in the formation of micronodules. Hence, micronodules originate in the host sediment. The subsequent compositional evolution of micronodules is governed by the nature of ferromanganese oxyhydroxide influx. During the discharge of submarine hydrothermal sources in the deep ocean water, primary ferromanganese oxyhydroxides are naturally depleted in Ce, Th, and Co, since the concentration of these elements in metalliferous sediments is low (Dubinin and Volkov, 1986, 1988; Migdisov *et al.*, 1979; Strekopytov, 1995).

Micronodules can originate simultaneously with the growth of a sediment microlayer, while the micronodule growth is a layer-by-layer process, and the transition to coarser fractions is gradual. It is less likely that a separate micronodule can autonomously attain the maximal dimension; otherwise, we should assume the possibility of polychronous micronodule formation within a single microlayer. The depletion of coarser micronodule fractions from horizons 165–175 and 189–190 cm in W, Th, and Co indicate that these micronodules include a purer hydrothermal material, relative to the smallest micronodules. At horizons 37–40 and 105–110 cm, larger micronodules are increasingly enriched in hydrogenic elements (Ce, Th, and Co) as a result of the abundance of hydrogenic oxyhydroxide in the suspended material. The close relationship between the hydrogenic (or hydrothermal) material concentration and micronodule dimension shows that micronodules preferentially derive these elements directly from suspended particulates of ferromanganese oxyhydroxides rather than from host sediments. The buried macronodules, which are characterized by largest dimensions, are most enriched in the hydrogenic Ce. The data on Th distribution in macronodules are lacking, and Ce is likely to be the least mobile element during diagenesis. Together with Mn, Ce^{4+} enters the suspended material. However, in contrast to Co, Ce is not transferred to solutions during the possible reduction on sediments or suspended particulates.

Figure 2 shows the fraction mass versus micronodule dimension relationship. It is evident that the fraction distribution at different horizons is variable. Based on the assumption that micronodules represent spheres, we can use a simple formula $m = \rho \times V \times n$ (m designates the micronodule mass in a fraction, ρ is the density, and V is the spherical micronodule volume) and calculate the number of micronodules (n) in the fraction. The average diameter of a micronodule is taken equal to the half interval between fraction sizes. The size of the 50- to 100- μ m-fraction micronodules, for example, will be equal to 75 μ m. Actually, it is not exactly correct; however, such assumption is valid for our calculations, since the error is insignificant. We accepted the micronodule density equal to that of ferromanganese nodules, i.e., 1.7 g/cm³ (Shishkova, 1989). Based on these assumptions, the number of micronod-

ules decreases with increasing dimension in the following way: 180742 $\rightarrow$ 83402 $\rightarrow$ 1093 $\rightarrow$ 5 (horizon 189–190 cm) and 312027 $\rightarrow$ 188273 $\rightarrow$ 18797 $\rightarrow$ 696 (horizon 37–40 cm). At both horizons, the fraction mass distribution is different but the number of micronodules rapidly decreases. In the second scenario, however, the possibility of a fast increase in micronodule dimension is much higher. The relationship between micronodules of similar fractions at horizons 37–40 and 189–190 cm changes in the following order: 2 $\rightarrow$ 2 $\rightarrow$ 17 $\rightarrow$ 129. The comparison of lower and upper horizons shows that the micronodule growth can be governed by the hydrothermal or hydrogenic oxyhydroxide type. It is also common knowledge that the number of micronodules in sediments inversely correlates with the sedimentation rate (Sval'nov, 1991). Hence, based on the micronodule mass distribution between fractions, one can assert that the sedimentation rate decreased upward the core in the study region.

The micronodule growth rate is determined by the rate of lithic material supply, while the composition is governed by the direct precipitation of ferromanganese oxyhydroxides from the near-bottom water. These conditions are realized for micronodules in the uppermost layer of liquid mud, where the labile fraction of newly formed mud is utilized and the oxyhydroxide suspension can directly precipitate on the micronodule surface. At the first stage, the micronodule can accommodate iron oxyhydroxide, which represents a halmyrolysis product of pyroclastic materials and compositionally differs from hydrothermal and hydrogenic oxyhydroxides (Dubinin, 1998). This mechanism of micronodule formation is efficient in an organic-poor environment, i.e., in nonproductive zones of ocean. In productive zones, owing to the development of suboxidative diagenesis, the REE signature of micronodules evolves in the following direction: fine (hydrogenic) micronodules—coarse (diagenetic) micronodules—macronodules—host sediment (Dubinin and Sval'nov, 1996).

Based on the proposed mechanism of micronodule growth in oceanic nonproductive zones, we can propose the following scenario for micronodule formation in sediments. Micronodules originate at the water–bottom interface, where the labile organic matter is abundant (Wang *et al.*, 1998) and the sediment is water-saturated, i.e., in the uppermost layer. The predomination of the role of direct precipitation of suspended oxyhydroxide particulates in larger micronodules suggests that a portion of micronodules was oriented toward the near-bottom water. The micronodule growth is terminated (i.e., micronodules are conserved) as a result of overlapping of sediments by the lithic material and depletion of the labile organic material.

CONCLUSION

Based on the comprehensive study of eupelagic clays from Site 35 in the South Basin, anomalously

high REE concentrations in these sediments are related to their accumulation on ferrocalsium hydroxophosphates. This conclusion is supported by the P-Fe correlation in residues of the 1M $\text{NH}_2\text{OH} \cdot \text{HCl} + 25\% \text{CH}_3\text{COOH}$ and 3.5N H_2SO_4 leachates of sediments. This kind of relationship is observed in ferromanganese micronodules. The P-REE(III) correlation is registered in samples of micronodules and buried ferromanganese macronodules. Since the P content is higher in sediments, relative to micro- and macronodules, the aforesaid distribution pattern is retained for REE(III) as well.

The study of four horizons of sediments in the Pacific nonproductive zone revealed that micronodules in this region inherit the compositional signature of host sediments. Hence, the finest fraction of micronodules is formed from the sedimentary material at the early diagenetic stage. During the subsequent growth of micronodules, the role of suspended hydrothermal or hydrogenic material, which is not associated with host sediments, becomes increasingly dominant. This inference is based on the direct correlation of typical hydrogenic elements (Ce, Co, Th, and possibly W) with the micronodule dimension. The attenuation of the sediment-micronodule interrelation in larger micronodules can serve as evidence of the origination of micronodules in the uppermost sediment layer that is comparable in thickness with the micronodule size. The preservation of general regularities of micro- and macronodule formation makes it possible to assume that micronodules represent the initial stage of ferromanganese mineralization in the ocean.

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Sorption on Humic Acids as a Basis for the Mechanism of Primary Accumulation of Gold and Platinum Group Elements in Black Shales

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Abstract—In order to assess the contribution of sorption by complexation to the concentration of noble metals at early stages of the formation of their deposits in black shales, the sorption of Au(III), Pt(IV), Rh(III), Ru(IV), and Os(IV) ions was studied on ash-free preparations of humic acids (HA) separated from peat of the Tver region and marine sediment samples taken on the Peruvian shelf. Data on the nature and protolytic characteristics of oxygen-containing HA functional groups were obtained. It has been shown that carboxyl groups and phenol oxygroups, which ensure the HA complexation with ions of noble metals, are present in the HA structure. The dissociation constant values for HA carboxyl groups (pK_a) and the distribution function of these groups in their pK_a values have been established. It has been revealed that the pK_a value for both of the HA groups varies within two orders of magnitude: the average value is equal to 6.1 for HA from peat and 7.0 for HA from marine sediments. A fairly high and similar for both of the HA groups sorption capacity with respect to Au(III), Rh(III), Ru(IV), and Os(IV) ions was established in model experiments. It is equal to 320–350 mg g⁻¹ for Au, 100–110 mg g⁻¹ for Pd, 11–12 mg g⁻¹ for Rh, 16–19 mg g⁻¹ for Ru, and 23 mg g⁻¹ for Os. The study of platinum(IV) sorption revealed that humic acids from peat and marine sediments do not virtually sorb Pt(IV), and this observation is important for understanding genetic features of the formation of noble metal deposits in black shales. Based on sorption isotherms for Au(III), Pd(II), Rh(III), and Ru(IV), the conditional affinity constant values for HA sorption centers with respect to ions of these metals were calculated by the method of quantitative physicochemical analysis. These values prove that complex compounds forming at the HA surface possess a high strength: the $\log \beta$ values for the Au(III)–HA, Pd(II)–HA, Rh(III)–HA, and Ru(IV)–HA compounds are equal to 6.0, 5.0, 3.2, and 3.5, respectively.

INTRODUCTION

The largest gold ore deposits of the world (Carlin in the United States, Witwatersrand in the Republic of South Africa, Muruntau in Uzbekistan, Kumtor in Kirgizia, and Sukhoi Log, Natalka, and others in Russia) are confined to sedimentary-metamorphic black shales. Problems concerning the Pt potential of black shales are intensely discussed in publications (Varshal *et al.*, 1994b, 1995, 1998b, 1998c; Distler *et al.*, 1996; Ermolaev *et al.*, 1995, 1999; Korobeinikov, 1999; Kurskii *et al.*, 1995; Mitrofanov *et al.*, 1994; Saraev and Pisarev, 1995; Chernyshev and Dodin, 1995; Yudovich and Ketris, 1994). The most important problem among them is the discrepancy by two to four orders of magnitude between the results obtained in the determinations of platinum group elements (PGE) in black shale samples accomplished with the use of most advanced, highly sensitive methods in leading analytical laboratories with highly qualified personnel (Varshal *et al.*, 1995, 1998b, 1998c; Kurskii *et al.*, 1995; Korobeinikov, 1999). This discrepancy of data has been caused by two interrelated phenomena: (1) specific features in

the PGE and Au distribution within noble metal deposits in black shales and (2) specific features in the mechanism of metal concentration during the formation of their deposits in sedimentary-metamorphic black shales. The mechanism includes the chemical interaction of noble metal compounds with the carbonaceous substance of rocks. A wide (as much as one to four orders of magnitude) range of the PGE and Au concentrations, a fairly high natural dispersion in the distribution of noble metals, as well as an increased level of the background concentrations of PGE and Au (as compared to their Clarke values in sedimentary rocks) are typical of these deposits (Varshal *et al.*, 1994a, 1995, 1998b, 1998c; Yudovich and Ketris, 1994).

Three possible processes responsible for the concentration of noble metals are considered in the framework of the mechanism of interaction of noble metal compounds with organic substances from marine sediments and products of their diagenesis and metamorphism. These processes are represented by reduction (Ong and Swanson, 1969), sorption resulting from the complexation of Au and PGE ions with functional

groups of organic substances (Baranova *et al.*, 1991; Bondarenko and Nechiporenko, 1986; Bondarenko *et al.*, 1984; Ermolaev *et al.*, 1999; Fisher and Fisher, 1984; Fridman *et al.*, 1982; Yudovich and Ketris, 1994; Radtke and Scheiner, 1970; Varshal *et al.*, 1990, 1994a, 1994b, 1995, 1998a, 1998b, 2000; Vorontsov *et al.*, 1984), and biosorption (Mossman and Dexter Dyer, 1985).

According to the concept stating that carbonaceous substances of black shales are of the organic (exogenic) origin, they were formed as a result of diagenesis and metamorphism of humic acids (HA), which represent basic organic substances contained in soils, water suspensions, and fluvial and marine sediments. The content of humic acids in present-day marine sediments is assessed at a level of 0.003–9.16% (Romankevich, 1977). There are many oxygen-containing functional groups in the HA structure, carboxyl groups and phenol oxygroups being basic among them. Their presence is responsible for the HA barrier function with respect to ions of Au, PGE, U, Th, REE, Cu, and other metals that can form stable complex compounds with oxygen-containing functional groups (Varshal *et al.*, 1999). The sorption on HA by the mechanism of complexation is likely to be the major process in metal concentration at early stages of the formation of gold and PGE deposits in sedimentary-metamorphic black shales. The results of model and field experiments with marine sediments and humic acids separated from these sediments and peats revealed a decisive role of humic acids in the accumulation of noble metals, such as gold (Baranova *et al.*, 1991; Varshal *et al.*, 1994b; Ermolaev *et al.*, 1999; Pashkova *et al.*, 1989; Fisher and Fisher, 1984), silver (Bondarenko and Nechiporenko, 1986), and palladium (Bondarenko *et al.*, 1991). According to (Fisher and Fisher, 1984), the capacity of marine silt for Au may attain 100 g t^{-1} . Humic acids represent the basic component, which is responsible for Au sorption, in organic matter of marine silt.

All these data are generally qualitative and confirm in principle the notion that the primary accumulation of Au and PGE during the formation of noble metal deposits in black shales is related to the chemical interaction of compounds of these elements with humic acids.

In order to quantitatively evaluate the strength of chemical bond of Au and PGE ions with humic acids, we need data on the nature and protolytic characteristics of oxygen-containing HA functional groups, as well as data on the HA sorption capacity with respect to noble metal ions. The strength of chemical bond between metal ions and humic acids can be evaluated by methods of the quantitative physicochemical analysis (Kholin, 1997). We can calculate the conditional affinity constants of oxygen-containing HA functional groups with respect to noble metal ions from sorption isotherms. The reliable quantitative information regarding the strength of chemical bond between metal ions and humic acids can only be obtained on the basis

of ash-free or low-ash preparations of humic acids with clearly characterized properties in sorption experiments.

The purpose of the present work was to study the properties of ash-free preparations of humic acids separated from marine sediments and peat by means of specially developed methods, establish the protolytic characteristics of oxygen-containing functional groups of humic acids, obtain the data on HA sorption capacity with respect to Au(III), Pt(IV), Pd(II), Rh(III), Ru(IV), and Os(IV) ions in model experiments, and calculate the conditional affinity constants of HA functional groups with respect to noble metal ions from sorption isotherms.

METHODS

Humic acids separated from marine sediments taken on the Peruvian shelf during the 14th cruise of the R/V *Dmitrii Mendeleev* and kindly placed at our disposal by A.A. Migdisov, as well as humic acids separated from peat of the Tver region were chosen as the objects of investigation. The procedure of separating ash-free HA preparations from peat was developed by the authors. It comprises the treatment of 10 weighed portions of peat having the mass up to 100 g with the 0.1 M solution of NaOH, the separation of alkaline solutions through filtration, and the subsequent HA precipitation by coagulation at the acidification of solutions with hydrochloric acid up to pH 1.0–1.5. Humic acids were decalcified by threefold treatment with the 5% solution of HF, then with the 2% solution of HCl, and the subsequent rinsing with distilled water up to the complete removal of chloride ions (Varshal *et al.*, 1996).

The procedure of HA separation from sediments taken on the Peruvian shelf substantially differed from the above-described one in the technique and temperature regime of sample treatment. The mixed sample of sediments having the mass 200 g was uniformly (25–30 g portions) distributed in eight glasses, each having a holding capacity of 1 l. The samples were poured with 700–800 ml of the 0.1 M solution of NaOH and heated to 55–60°C. The HA solutions were separated through filtration. The procedure of alkaline treatment of each precipitate was repeated eight times. The filtrates were united and humic acids were separated through coagulation at the acidification of alkaline solutions with hydrochloric acid up to pH = 1.0–1.5. The major portion of the solution was poured off by decantation, and the HA precipitate from all eight extracts were united. The precipitate of HA after its separation by centrifuging at 3000 rpm was transferred to glass-graphite cups and decalcified through the successive threefold acidic treatment in accordance with the above described procedure. The obtained HA preparations were air-dried and grinded. The ash content of final preparations was 0.22% for HA from peat and 0.84% for HA from marine sediments.

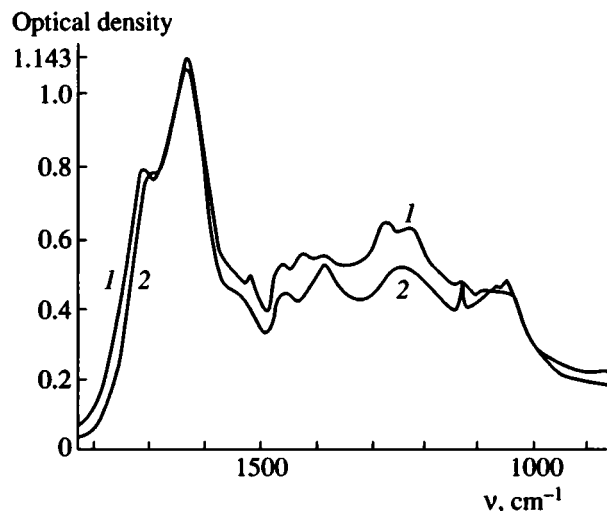


Fig. 1. IR absorption spectra of (1) humic acids separated from peat and (2) marine sediments.

The properties of humic acids were studied by the potentiometric titration, IR spectrometry, CHNS analysis, and X-ray diffraction analysis.

The potentiometric titration of HA was performed using the method of treatment of separate weighed portions by CO_2 -free aqueous solutions of KOH. Weighed portions of humic acids with a mass of 20 mg were placed into a series of cylindrical Teflon vessels having a holding capacity of 40–50 ml and equipped with screw-on caps. From 0 to 4.5 ml of the 0.0126M solution of KOH (CO_2 -free) were added in each of these vessels, and then distilled water was poured until the total volume attained 20 ml. After filling the vessels with argon, they were placed into the ABU-1 apparatus for shaking. Aliquot portions of solutions for the pH measurement were taken after 5 h and 1, 2, and 5 days.

In the sorption experiments, we used solutions of chloride complexes of noble metals obtained by dissolving in aqua regia the weighed portions of chloroauric acid (for Au), platinum wire (for Pt), palladium dichloride (for Pd), and rhodium trichloride (for Rh). For all weighed portions, the treatment with aqua regia was repeated three times, whereupon the solutions in glasses were evaporated to moist salts. The treatment of the obtained material with water and hydrochloric acid and the evaporation to moist salts were repeated three to seven times. The content of glasses was diluted with water, and the acidity of solutions was regulated up to pH 5 using the 1M and 0.1M solutions of NaOH. In the study of sorption of Ru(IV) and Os(IV) on humic acids, the solutions of potassium oxo-bis-pentachlororuthenate at pH = 2.2 and potassium hexachlorosmate at pH = 2.9 were used as the starting compounds of these elements. For each of the metals, a series of solutions of their chloride complexes were prepared with a progressively growing concentrations (on the metal basis): Au from 49 to 442 $\mu\text{g ml}^{-1}$, Pt from 17 to 316 $\mu\text{g ml}^{-1}$, Pd

from 21 to 381 $\mu\text{g ml}^{-1}$, Rh from 10 to 150 $\mu\text{g ml}^{-1}$, Ru from 10 to 200 $\mu\text{g ml}^{-1}$, and Os from 10 to 250 $\mu\text{g ml}^{-1}$.

The technique of sorption experiments was as follows. Twenty ml of each solution were added to the weighed portions of HA (20 mg) in cylindrical Teflon vessels with a holding capacity of 40–50 ml. After meticulous stirring, aliquot portions of the solutions were taken during the 1st, 2nd, 3rd, 4th, and 7th days for determining Au and PGE concentrations by the AES-ISP method on an ICAP-61 polychromator (Thermo Jurrel Ash Corp.).

The data on the content of carbon, hydrogen, nitrogen, and sulfur in ash-free HA preparations were obtained using the CHNS analyzer, Carlo Erba (Italy). The IR absorption spectra of HA were recorded in the frequency range from 500 to 3700 cm^{-1} on a PU-9800 FTIR-spectrometer. The HA structure was investigated on a DRON-4 X-ray diffractometer. The contribution of aromatic and aliphatic structures was evaluated from the XRD data by decomposing the experimental diffractograms into individual peaks using the Lorentz form functions (Varshal *et al.*, 1995). The data on the HA sorption capacity with respect to noble metal ions were obtained from sorption isotherms. The values of conditional affinity constants for HA sorption centers with respect to noble metal ions were calculated from the same isotherms by the method of quantitative physicochemical analysis (Kholin, 1997).

RESULTS AND DISCUSSION

The IR absorption spectra of humic acids separated from peat (curve 1) and marine sediments (curve 2) are presented in Fig. 1. It can be seen that the IR spectra of humic acids from both peat and marine sediments are fairly similar. They comprise a very intense absorption band in the 1605–1630 cm^{-1} region related to stretching-region asymmetric oscillations of ionized carboxyl groups. A sufficiently intense absorption band at 1700–1720 cm^{-1} caused by stretching-region asymmetric oscillations of nonionized carboxyl groups is clearly pronounced. The intense absorption band at 1040–1050 cm^{-1} , which is typical of oxygroups, is observed in the spectra of both humic acids. Hence, both carboxyl and phenol oxygroups, which ensure the formation of stable complex compounds with ions of noble and many other metals at the HA surface are present in the HA structure.

The pH-metric titration of ash-free HA preparations was performed using the method of separate weighed portions with CO_2 -free aqueous solutions of KOH. It was found that the equilibrium in the heterophase (HA–titrant solution) systems is established in two days. Three distinct peaks are generally observed on the differential curve of potentiometric titration of humic acids from peat (Varshal *et al.*, 1998a). Two peaks can be seen on the curve of potentiometric titration of humic acids from marine sediments (Fig. 2). The disso-

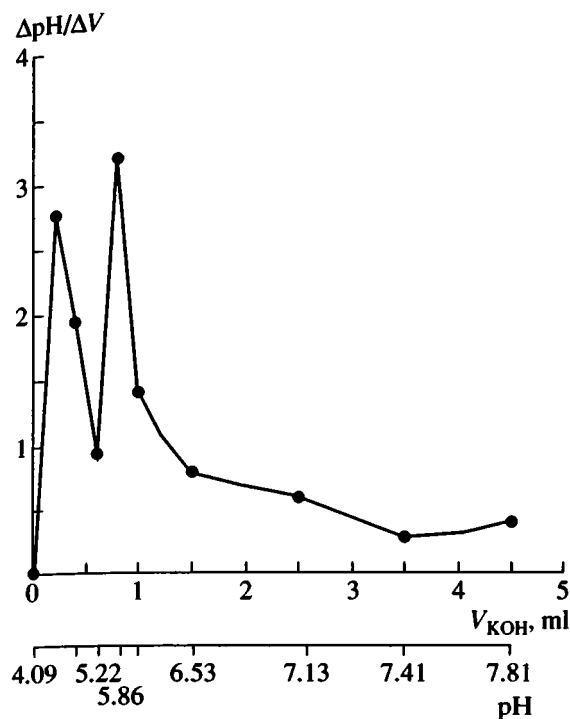


Fig. 2. Differential curve of the potentiometric titration of humic acids separated from marine sediments. $m_{\text{HA}} = 20 \text{ mg}$; $C_{\text{KOH}} = 0.0126 \text{ M}$; solution volume 20 ml.

ciation constant values for HA functional groups (pK_a) were established from the data of the pH-metric titration by the methods of quantitative physicochemical analysis (Kholin, 1997). The transformed Langmuir equation with the calculation of isotherm parameters by the nonlinear method of least squares in accordance with the CLINP 1.0 program was used for this purpose. The energy inhomogeneity of HA functional groups was calculated using the CAS algorithm of distribution functions of nondissociated functional groups versus dissociation constant indices. According to (Varshal *et al.*, 1998a), the pK_a value for the peat-derived HA carboxyl groups varies from 5.0 to 7.0 (average 6.1). Figure 3 shows that the pK_a value for HA carboxyl groups from marine sediments varies from 6.0 to 8.0 (average 7.0). One can see that the distribution of functional groups versus dissociation constant indices is in agreement with the Gauss distribution.

The diffractograms of ash-free HA preparations from peat of the Tver region and marine sediments of the Peruvian shelf are illustrated in Fig. 4. The principle of decomposition of the experimental diffractograms into individual peaks calculated by means of the Lorentz form functions (Varshal *et al.*, 1995) is also shown in the figure. Based on these data, the contributions of aliphatic and aromatic structures to the HA structure are equal to 77.2 and 22.8%, respectively, for humic acids from peat and 66.0 and 34.0%, respectively, for humic acids from marine sediments. The

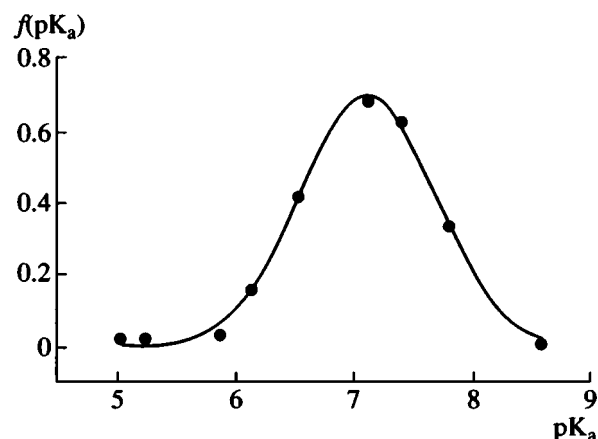


Fig. 3. Distribution function of nondissociated carboxyl groups of humic acids from marine sediments vs. pK_a values.

results of elemental analysis of humic acids are presented in Table 1.

The sorption of Au(III), Pt(IV), Pd(II), Rh(III), Ru(IV), and Os(IV) ions in the form of their chloride complexes on ash-free HA preparations separated from peat and marine sediments was studied in model experiments. The obtained results showed that the equilibrium in the HA-PGE ions system is established during the time from 2 h to 1 day, and the equilibrium in the Au(III)-HA system is established in 7 days. Sorption isotherms of Au(III), Pd(II), and Rh(III) on humic acids from peat and marine sediments at $\text{pH} = 5.0$ are depicted in Figs. 5–7. Sorption isotherms of Ru(IV) at $\text{pH} = 2.2$ and Os(IV) at $\text{pH} = 2.9$ on humic acids from peat of the Tver region are presented in Fig. 8. The data obtained convincingly demonstrate that humic acids from both peat and marine sediments have a fairly high and similar sorption capacity with respect to Au(III), Pd(II), and Rh(III) ions. In humic acids from peat, the sorption capacity is 320 mg g^{-1} for Au, 100 mg g^{-1} for Pt, 11 mg g^{-1} for Rh, $16\text{--}19 \text{ mg g}^{-1}$ for Ru, and 23 mg g^{-1} for Os. In humic acids from marine sediments, the sorption capacity is 351 mg g^{-1} for Au, 110 mg g^{-1} for Pd, and 11.6 mg g^{-1} for Rh.

A very interesting phenomenon was revealed in the study of Pt(IV) sorption. In contrast to other coal-bearing substances, such as coals, carbonaceous particles of rocks, and bitumens, humic acids from peat and marine sediments, practically do not sorb Pt(IV) (Varshal *et al.*, 1994a, 1994b, 1995, 1998b, 1998c, 2000). The reasons for this phenomenon are complicated and call for addi-

Table 1. Results of the CHNS analysis of humic acids, %

Sample characteristics	C	H	N	S
HA from peat	51.26	5.20	1.55	0.24
HA from marine sediments	50.57	6.08	2.72	traces

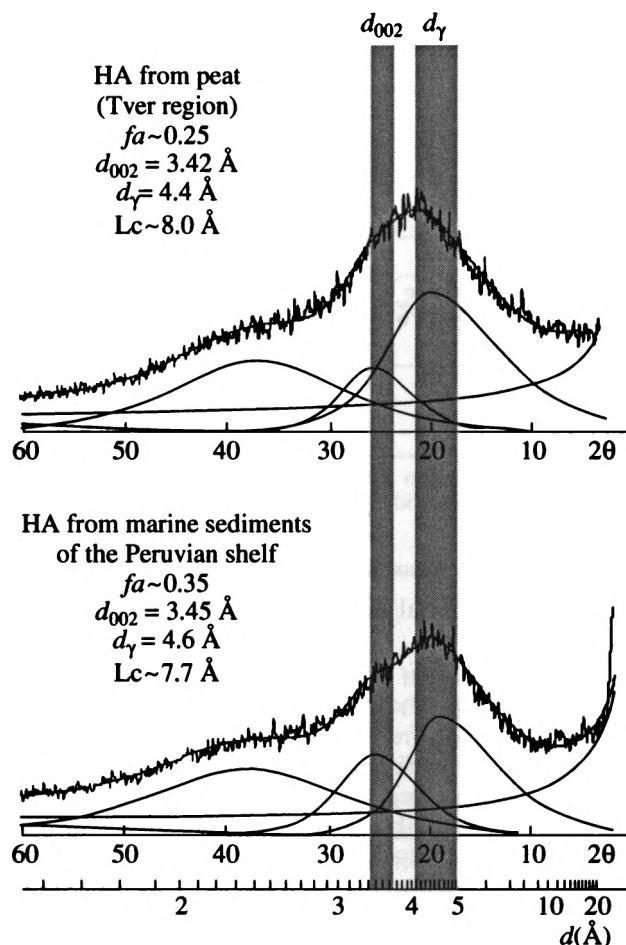


Fig. 4. Diffractograms of humic acids separated from peat and marine sediments. Vertical dashed lines indicate the spatial intervals typical for the aromatic (d_{002}) and aliphatic (d_γ) structures.

tional investigations. It follows from the data of model experiments that the sorption on humic acids from marine sediments can be crucial for the accumulation of Au, Pd, Rh, Ru, and Os at early stages of the formation of noble metal deposits in carbonaceous sequences. However, the probability of Pt accumulation during these processes is not large. Therefore, the intense search for Pt in black shales is unlikely to be justified. The critical consideration of published data on high Pt contents in black shales is also necessary. Most commonly, the overestimation of data on Pt contents results from analytical errors related to the influence of numerous associated elements.

The processing of data on the sorption of Au and PGE ions by the methods of quantitative physicochemical analysis has made it possible to evaluate the strength of chemical bond between metal ions and HA sorption centers. The sorption of Au(III), Pd(II), and Rh(III) on HA from peat and marine sediments can be satisfactorily described by the Langmuir isotherm

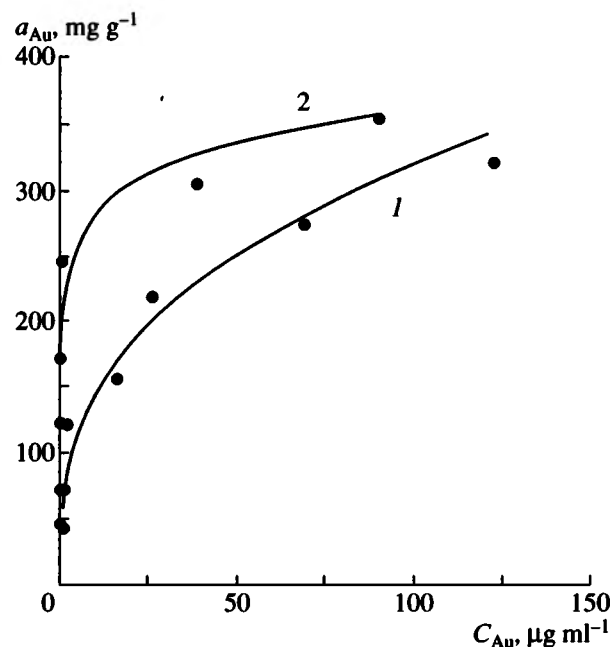


Fig. 5. Sorption isotherms of Au(III) on humic acids. (1) HA separated from peat; (2) HA separated from marine sediments. pH = 5.0; $m_{HA} = 20$ mg; $V = 20$ ml.

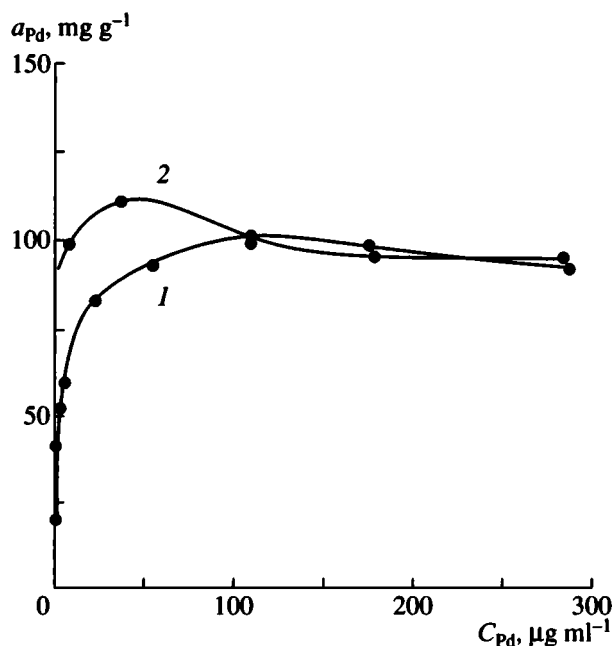


Fig. 6. Sorption isotherms of Pd(II) on humic acids. (1) HA separated from peat; (2) HA separated from marine sediments. pH = 5.0; $m_{HA} = 20$ mg; $V = 20$ ml.

equation. The calculation of isotherm parameters by the nonlinear method of least squares yielded the values of conditional affinity constants of HA sorption centers with respect to noble metal ions (Table 2). These constants represent a quantitative characteristic of the chemical bond strength between metal ions and HA

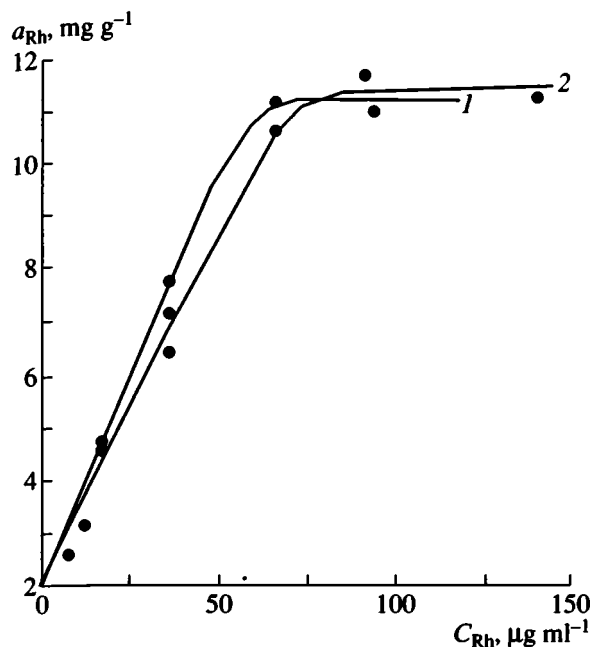


Fig. 7. Sorption isotherms of Rh(III) on humic acids. (1) HA separated from peat; (2) HA separated from marine sediments. pH = 5.0; m_{HA} = 20 mg; V = 20 ml.

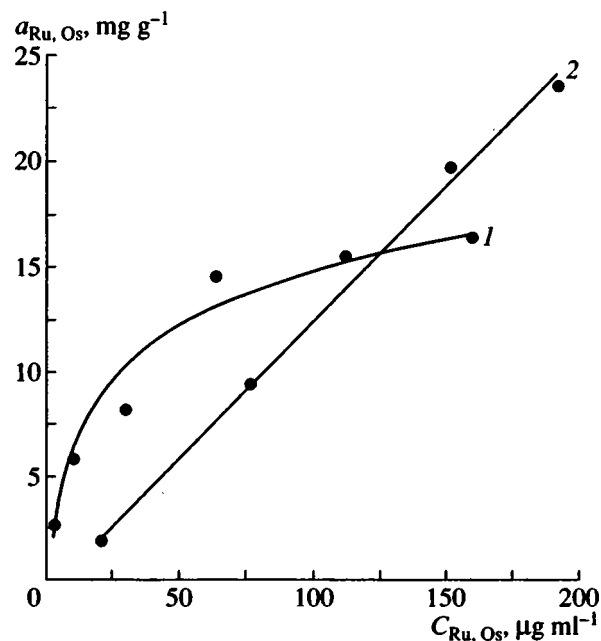


Fig. 8. Sorption isotherms of (1) Ru(IV), pH = 2.2 and (2) osmium(IV), pH = 2.9 on humic acids separated from peat of the Tver region.

functional groups. Calculations based on the CAS algorithm of distribution functions of HA sorption centers versus logarithms of conditional affinity constants with respect to ions of each metal showed that these functions are in agreement with the Gauss distribution functions. The energy inhomogeneity of HA functional groups at the sorption of metal ions (Table 2) is not practically manifested.

The chemical bond strength is the parameter that determines the ratio of coexisting forms of noble metals in coal-bearing rocks and the possibility of their quantitative recovery for technological or analytical purposes. The chemical bond of noble metal ions with the carbonaceous matrix is retained until oxygen-containing functional groups are present in the structure of carbonaceous substances. The diagenesis and metamorphism of organic substances accompanied by their decarboxylation and the subsequent diminishing of the

number of oxygen-containing functional groups, along with the reduction of the sorption capacity and strength of chemical bond of Au and PGE ions with the carbonaceous matrix. Consequently, the separation and redistribution of Au and PGE becomes possible, resulting in the appearance of fine-dispersed elemental forms and mineral forms, such as sulfides, tellurides, selenides, metals incorporated in metallic solid solutions, and others, which actually coexisting in black shales.

CONCLUSION

Noble metal deposits in sedimentary-metamorphic black shales play an important role as a new nontraditional source of Au and PGE. Problems of the genesis of such deposits are very complicated. Their formation is primarily governed by the chemical interaction of noble metal ions with the basic organic substance of marine sediments (humic acids) and products of their diagenesis and metamorphism. This interaction follows the mechanism of complexation of Au and PGE with oxygen-containing functional groups of humic acids. The sorption on humic acids as a natural complexing sorbent is the main mechanism responsible for the primary accumulation of noble metals during the formation of polymetallic deposits in carbonaceous sequences.

To prove these statements, we scrutinized the sorption of Au(III), Pt(IV), Pd(II), Rh(III), Ru(IV), and Os(IV) ions on ash-free HA preparations from peat and marine sediments and obtained data on the nature and protolytic characteristics of oxygen-containing HA

Table 2. Conditional affinity constants of HA sorption centers with respect to Au(III) and PGE ions

Metal ion	log β	
	for HA from peat	for HA from marine sediments
Au(III)	4.4	6.0
Pd(II)	4.7	5.0
Rh(III)	3.4	3.2
Ru(IV)	3.5	

functional groups. Based on model experiments, humic acids from peat and marine sediments have a fairly high sorption capacity with respect to ions of all the investigated noble metals, except Pt. The sorption capacity is 320–350 mg g⁻¹ for Au, 100–110 mg g⁻¹ for Pd, 11–12 mg g⁻¹ for Rh, 16–19 mg g⁻¹ for Ru, and 23 mg g⁻¹ for Os. The values of conditional affinity constants of HA sorption centers with respect to Au and PGE ions prove the high strength of newly forming complex compounds. All these data undoubtedly point to a decisive role of sorption concentration in the primary accumulation of Au and PGE in black shales. Model experiments with the Pt(IV)–HA system also revealed that in contrast to other coal-bearing substances (coals, carbonaceous particles of rocks, bitumens, and others), humic acids from peat and marine sediments practically do not sorb platinum. Therefore, one should regard with great caution numerous published data on the high Pt content in coal-bearing rocks.

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Diagenetic Mineral Formation in Biogenic Structures (Paleogene, Northeastern Caucasus)

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Abstract—Rare biogenic structures, after which diagenetic minerals are developed, are described from Paleogene rocks of southern Dagestan. It is shown that these minerals form tabular mica-like and colloform aggregates confined to fucoids. In terms of composition, they represent the glauconite group minerals. Tabular and colloform minerals are compared with globular glauconite occurring in host sandy rocks. It is demonstrated that the globular variety is characterized by higher K and Fe contents, whereas the tabular variety has a higher SiO_2 content. The probable mechanism of the formation of tabular and colloform minerals in biogenic structures is discussed.

INTRODUCTION

The study of authigenic mineral formation in coeval rocks developed over a large territory makes it possible to assess diagenetic transformations depending on changing facies environments. In this respect, Paleocene–Eocene rocks of the Caucasian region, which are mainly composed of mixed biogenic–terrigenous sediments, represent a favorable study object. At the sedimentation and diagenesis stages, they contained a noticeable amount of primarily basinal organic matter (OM), which promoted active diagenetic processes. Paleocene–Eocene rocks developed in different areas enclose various (authigenic diagenetic) formations, such as abundant sulfide nodules, common phosphate, carbonate, siliceous, and barite concretions, as well as small authigenic aggregates (phosphate grains and zeolite crystals).

The study of rocks in the South Dagestan Facies Zone revealed that they are characterized by an elevated intensity of silicate diagenetic mineralization owing to a high bioproductivity of siliceous organisms in this part of the paleobasin. In carbonate-dominated sediments (the Rubas-chai River section), the diagenetic redistribution of biogenic silica resulted in the formation of numerous nodules and lenticular interbeds mainly composed of SiO_2 , whereas terrigenous sequences are characterized by a wide development of the glauconite-group minerals up to the point of the formation of glauconite interbeds associated with hardgrounds at some levels.

In the lower Eocene sequence, we discovered biogenic structures, which enclose authigenic phyllosilicate minerals with some slightly unusual parameters. These biogenic structures, which resulted from the life activity of some organisms, are sufficiently rare and confined to sediments of certain facies environments. The aim of this work is a comprehensive study of these

biogenic structures, including their description, establishment of their origin, elucidation of the composition of authigenic minerals confined to these biogenic structures, and their comparison with similar minerals occurring in host sediments.

CHARACTERISTICS OF BIOGENIC STRUCTURES AND HOST SEDIMENTS

The section of mainly carbonate and clayey–carbonate Paleocene–Eocene sediments of southern Dagestan (the Rubas-chai River) includes a sequence of fine-grained, light-colored and compact carbonate sandstones, about 40 m thick. At some levels, the sandstones are silicified. According to (Shutskaya, 1970; Muzylev, pers. communication), the sandy sequence is referred to the lower Eocene (Ipresian).

The sandstones are characterized by subhorizontal and gently wavy bedding formed by alternating thin (several millimeters), gray and white laminae mainly composed of clastic silicate material and biogenic calcareous mud, respectively. The bedding is locally disturbed by bioturbation.

The clastic silicate material is represented by angular quartz grains (30–50 vol %) with an admixture of feldspars (up to 10 vol %). Biogenic components make up about 50 vol % of the rock with sharply dominant and variably recrystallized carbonate foraminiferal tests. Both silicate and biogenic components of the rock are well sorted and dominated by grains 0.1–0.2 mm in size.

The sandstones contain dispersed glauconite globules (not more than 10 vol %). Most globules are localized within laminae of a clastic silicate material. Dimensions of glauconite grains (0.1–0.2 mm) are close to those of the major clastic components.

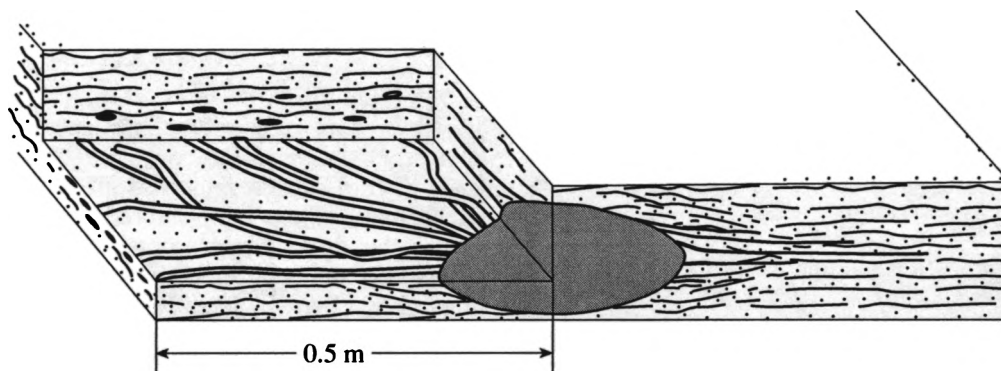


Fig. 1. A sketch image of the biogenic structure from lower Eocene sandstones of southern Dagestan (Rubas-chai River area).

The sandstone cement is mostly composed of a basal, crystalline carbonate material (calcite with an insignificant admixture of ankerite). Biogenic laminae sometimes enclose sufficiently large areas cemented by a micritic carbonate substance. The sandstones contain thin cracks filled by fibrous chalcedony and microporous opal.

At several levels, the sandstones enclose very unusual siliceous lenses with radial, slightly curved, and diverging dark green bands (Fig. 1). The lenses represent flattened compact nodules with an uneven surface dissected by cracks with chalcedony sinters. The nodules, up to 20–25 cm across and 4–5 cm thick, are characterized by an irregular, ocherous yellow to black color. The divergent, narrow (1–2 cm), slightly wavy, radial bands, 30–40 cm long, locally intersect and gradually wedge out. The band-shaped channels approach siliceous lenses at different levels and sometimes envelope the lenses (Fig. 1). On the plane, which is perpendicular to the axis of bands, the channels resemble strongly flattened (1–2 mm thick) and short (a few centimeters) lenses located at different levels and filled by a green or dark green mineral substance. In some cases, the small lenses have the form of flattened ellipses, up to 5–6 mm thick. If the channels are oblique to the bedding surface, they acquire an almost rounded shape.

The microscopic study of the internal structure of nodules reveals that they represent accumulations of microcoprolites (Fig. 2) locally enriched in small foraminiferal tests. All components are completely replaced and compactly cemented by a homogeneous, microspherulitic silica aggregate with an irregular impregnation of fine-dispersed iron sulfides, which emphasize primary forms of biogenic components. Every separate nodule together with the system of diverging narrow bands represent a genetically single biogenic structure. Bromley (1996) reported a series of similar radiating burrow systems registered both in recent and ancient sediments. Most of them, however, are characterized by smaller dimensions. For instance, the considered formations show some morphological and dimensional similarity with biogenic structures

reported by Bromley and Asgaard (1972) from Jurassic fine- and medium-grained sandstones of eastern Greenland. They interpreted the structures as living chambers of crustaceans, which could freely move within sediments, and diverging channels as tunnels, through which organisms could penetrate into sediments and back. Main differences between southern Dagestan and eastern Greenland biogenic structures are related to their fossilization patterns. In the eastern Greenland burrow systems, channels diverging from the central

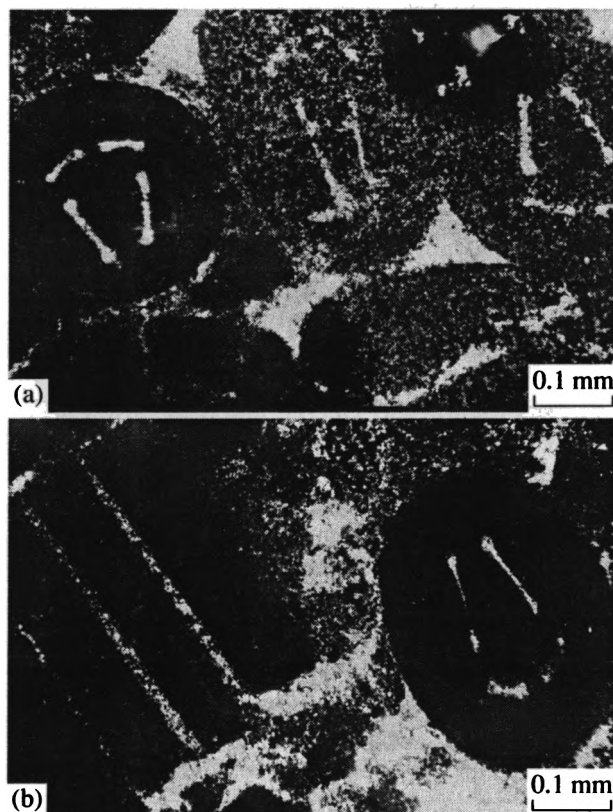


Fig. 2. Microphotographs of coprolites from the siliceous lens and their internal structure.

chamber are filled with a material of host sediments and the initial appearance is significantly preserved (the authigenic mineralization was not registered). In our case, the channels did not practically preserve their primary form, since they were significantly flattened and filled by newly formed green-colored authigenic minerals.

Coprolites are often abundant in the studied rocks (Khvorova, 1953; Maslov, 1960; and others). One should know their morphology and internal structure to understand their origin. Coprolites discovered in the Ipresian rocks represent small (less than 1 mm) cylindrical bodies randomly distributed throughout the rock mass (Fig. 2). They are crosscut by four drainage (according to the terminology of O.S. Vyalov) channels located symmetrically to the main axis. In modern coprolites of such type, channels are formed by finger-like protrusions from the rear end of an animal stomach (Vyalov, 1978).

The study of the internal structure of coprolites, which are localized in the siliceous lens representing the central part of the biogenic structure, allows organisms responsible for their formation to be established with a sufficient confidence. Coprolites with an identical or similar internal structure were recorded in Jurassic rocks of England (Kennedy *et al.*, 1969), Lower Cretaceous sections of Hungary (Palik, 1965), and Triassic, Jurassic, and Cretaceous rocks of North Africa and Europe (Brönnimann, 1972; Brönnimann and Zaninetti, 1972; Brönnimann *et al.*, 1972). Similar microfossils were also reported by Maslov (1960) from Tertiary rocks of the Tadjik Depression. All data on coprolites available at that time are given in the Atlas of rock-forming organisms (Maslov, 1973). Vyalov (1978 and others) found similar coprolites in Turonian rocks in the Amudar'ya River area. In the Caucasian region, similar but not identical microfossils were registered in phosphate concretions within clays of the Goryachii Klyuch Formation (upper Paleocene) of the central Caucasus (Senowbari-Daryan and Silantiev, 1991). In all cases, researchers considered coprolites of this type as a product of the life activity of Decapoda (Crustacea) representatives. Therefore, the formation of biogenic structures and associated coprolite accumulations in the study region should also be considered as a result of the life activity of these organisms.

Sometimes, researchers note the presence of green minerals in crustacean (Decapoda) burrows, which were referred to glauconite, although their composition was not studied (Bromley and Asgaard, 1972; and others). With respect to some characteristics, the green minerals, which we observed in burrows, are somewhat unusual. That is why we performed special studies of their composition and compared them with glauconite in host rocks.

CHARACTERISTICS OF AUTHIGENIC MINERALS

Minerals filling burrows are mainly represented by relatively soft, dark green aggregates, which usually cover their inner surface over the entire length in the form of film or thin crust and are distinct against the background of the light-colored enclosing sediments. Under the optical microscope, the thin (millimeter-scale) lenses are observed as tabular mica-like structures (Figs. 3a, 3b) usually enveloping grains of the enclosing rock. Sometimes, they include small calcite crystals, quartz grains, and globular glauconite (the glauconite grain is indicated by an arrow in Fig. 3a). In thicker burrows, the filling mineral material shows a zonality. The peripheral part of the channel is mostly composed of a dark green mica-like mineral, which acquires blue color toward the central part. Tabular patterns are gradually replaced by less regular, macroscopic colloform mineral mass.

Plates usually reveal strong pleochroism varying from the yellowish white to intense dark green color with a domination of the mica-type interference colors. Less common are aggregates with poor pleochroism, less bright interference colors, and undulatory extinction.

Globular glauconite from enclosing sandstones is mainly represented by isometric (or elongated and rounded) dark green grains with a smooth or slightly uneven surface. Some globules have an irregular form with highly smoothed edges. In thin sections, they are characterized by a uniform and intense green color, which does not practically change under crossed nicols, and a chaotic internal structure of microaggregates.

Authigenic minerals were studied with the application of the high-resolution scanning electron microscopy, X-ray and electron-diffraction methods, along with quantitative microprobe and chemical analyses. We studied the dark green tabular (Sample 3011/3t) and light bluish green colloform (Sample 3011/3c) aggregates from biogenic structures, as well globular glauconites from enclosing sandstones (Sample 3011/3g). To obtain monomineral preparations for the SEM study of the nanotexture, tabular aggregates were picked by hand. The same samples were also used for microprobe investigation.

Inasmuch as the admixture of globular glauconite in sandstones does not exceed 10%, their 0.1–0.2-mm fraction was concentrated approximately to 75–90% using electromagnetic separators. The nanotexture was studied in most characteristic globules. Using the X-ray diffraction method, minerals were analyzed in oriented preparations from the <0.001-mm fraction obtained by elutriation of the material enriched in glauconite globules. The microprobe analysis of statistically random globules was performed in the polished section of sandstones.

Nanotextural Features. Under the scanning electron microscope, transverse slices of *tabular mineral* reveal

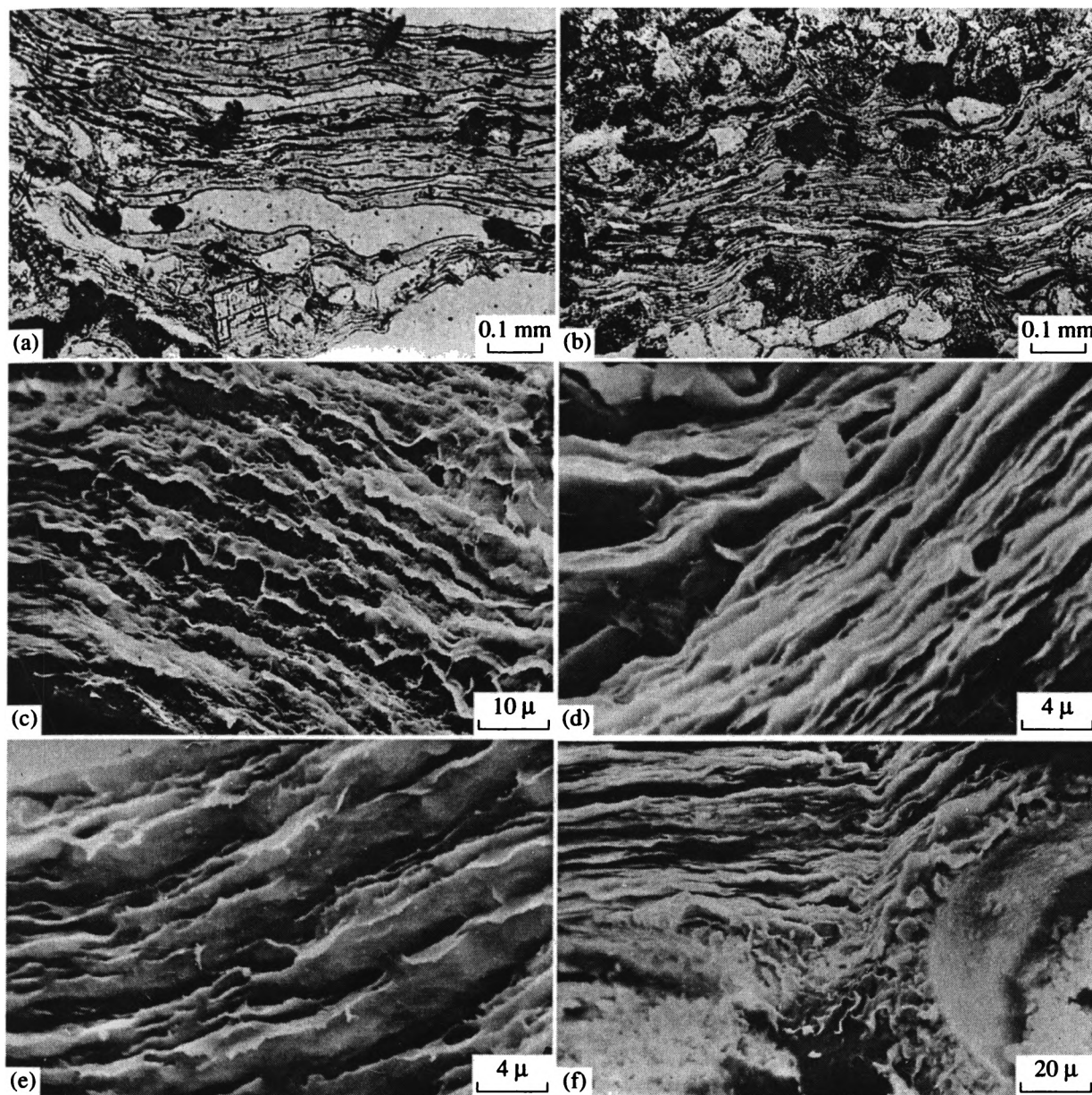


Fig. 3. (a, b) Microtexture and (c–f) nanotexture of a tabular mineral of the glauconite group. (a, b) Photomicrographs of the tabular mineral in thin section; the arrow in Fig. 3a indicates a globular glauconite grain sealed within the tabular mineral; (c–f) photomicrographs of the tabular mineral under the scanning electron microscope; 3f shows foraminiferal tests enveloped by glauconite scales.

a lamellar- and lepidoblastic-parallel texture (Figs. 3c–3f). The thickness of flakes and scales is $0.n \mu\text{m}$. The lepidoblastic-parallel texture is formed by relatively short ($2\text{--}5 \mu\text{m}$) and slightly curved scales overlapping each other, thus imparting an imbricate pattern to the texture (Fig. 3c). The lamellar-parallel texture is built by larger ($10n \mu\text{m}$) plates that are tightly, almost continuously arranged in the sample within the observation zone. Their edges are usually subparallel and relatively straight (Figs. 3d, 3e).

Under the scanning electron microscope, *colloform mineral aggregates* associated in fucoids with tabular

ones are characterized by a greater diversity of the nanotexture: both subparallel and chaotic varieties are present. The subparallel texture is formed by thickened restiform aggregates (Figs. 4a, 4b). Nonoriented textures (cellular- or honeycomb-type) are formed by a chaotic intergrowth of very small (less than $1 \mu\text{m}$) isometric curved scales (Figs. 4c, 4d).

Under the scanning electron microscope, *globular glauconite* is mostly characterized by a microrelief- and fissures-free smooth surface. The splinting surface reveals a chaotic intergrowth of rosette-, cluster-, and fan-shaped aggregates (Figs. 4e, 4f). Scales composing

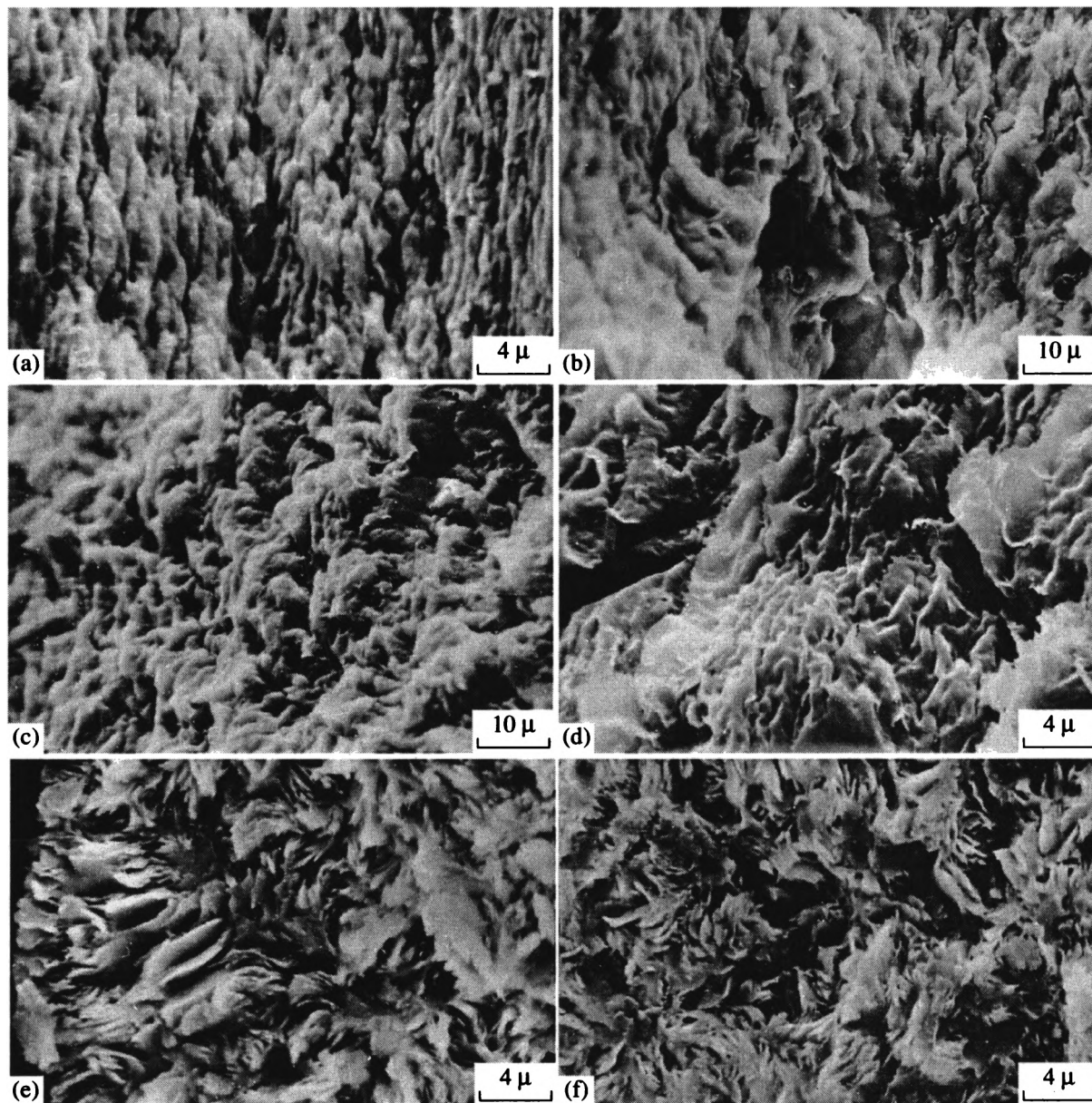


Fig. 4. Nanotexture of the (a–d) colloform mineral of the glauconite group and (e, f) globular glauconite from enclosing sandstones.

these aggregates are usually 1–2 μm in size. The similar texture is typical of globular glauconites and was described in many publications (Nikolaeva, 1977; Nikolaeva *et al.*, 1981; Lisitsyna and Butuzova, 1981; Odin *et al.*, 1988; Geptner and Ivanovskaya, 1998; and others).

The above-mentioned nanotextures of the tabular mineral were practically never described for authigenic, dioctahedral, Fe-rich micaceous minerals. In the opinion of Odin and Fullagar (1988), the elongated-tabular appearance of microcrystallites (up to 20 μm long and 0.2–0.3 μm thick) is typical of celadonite. However, SEM images of celadonite demonstrated in

the above work are devoid of nanotextures with a parallel arrangement of microcrystallites.

The internal texture of colloform segregations is probably transitional from lamellar- and lepidoblastic-parallel varieties with a distinct crystalline appearance to the less ordered and sometimes close to glauconite-type textures of globular structures.

Results of X-ray Diffraction Studies. In diffraction patterns, the natural tabular mineral is close to micas with an elevated Fe content (Fig. 5, Sample 3011/3t, a). The observed insignificant shift of the first basal reflection to the low angle region ($d_{001} = 10.50\text{--}10.70 \text{ \AA}$) and related slight distortion of the regularity of basal reflec-

tions imply the presence of swelling interlayers. It is noteworthy that the sample saturation with ethylene glycol results in the separation of the first basal reflection into two contiguous peaks: more intense peak with $d_{001} = 9.80\text{--}9.93\text{ \AA}$ and less intense one with $d_{001} = 10.80\text{--}11.00\text{ \AA}$ (Fig. 5, Sample 3011/3t, b), suggesting the alternation of mica and smectite layers with the short-range order factor $S \gg 1$ (Drits *et al.*, 1993). The comparison with theoretical diffraction patterns calculated for mixed-layer mica-smectite formations (Drits and Sakharov, 1976) showed that the studied mineral is closest to the mixed-layer phase of dioctahedral mica-smectite with the content of swelling layers not more than 10–15% and the short-range order factor $S = 3$, indicating the trend toward a relatively high ordering of the alternation of mica and smectite layers at the studied level of their proportions.

The elementary cell parameters of tabular mineral determined by the electron-diffraction method are as follows: $a = 5.24\text{ \AA}$, $b = 9.072\text{ \AA}$, and $c = 10.11\text{ \AA}$ at $\beta = 101.2^\circ$. These values correspond to the dioctahedral Fe-rich mica.

Diffraction patterns obtained for the colloform mineral reveal a phase heterogeneity (Fig. 5, Sample 3011/3c, a, b). Two mixed-layer Fe-rich mica-smectite phases with $d_{001} = 11.20\text{ \AA}$ are present as main components. This is inferred from the separation of the first basal diffraction into three contiguous peaks (more intense peak with $d_{001} = 9.8\text{ \AA}$ and two less intense ones with $d_{001} = 11.5\text{ \AA}$ and $d_{001} = 12.6\text{ \AA}$) owing to the presence of two mixed-layer mineral phases. They differ in the content of swelling layers and structural ordering degree. For instance, the first phase contains as much as 10–15% swelling interlayers with the short-range order factor $S = 3$ and is identical to the above-described phase of the tabular mineral, whereas the second phase contains up to 25% swelling interlayers with $S = 2$ (Drits and Sakharov, 1976). The sample also contains an admixture of organic-rich smectites, which are revealed by several weak reflections in the low angle region: $d_{001} = 14.70\text{--}18.00\text{ \AA}$ in the initial preparation and $d_{001} = 18.60\text{ \AA}$ in the preparation saturated with ethylene glycol.

Diffraction patterns obtained for the oriented preparation of sandstone fraction enriched in dark green globules correspond to those of quartz and Fe-rich mica with $d_{001} = 10.00\text{ \AA}$ (Fig. 5, Sample 3011/3g, a, b). When the preparation is saturated with ethylene glycol, the first basal reflection is only insignificantly shifted (up to $d_{001} = 9.98\text{ \AA}$), indicating the absence of swelling layers in the mineral structure and allows it to be interpreted as mica.

Chemical Composition of Minerals. The chemical characteristics of three morphological varieties of green phyllosilicates are presented in the table. The results are mainly based on the microprobe (Camebax) data. The tabular mineral was also subjected to silicate analysis. As is seen from the table, the Fe_{tot} i.e.,

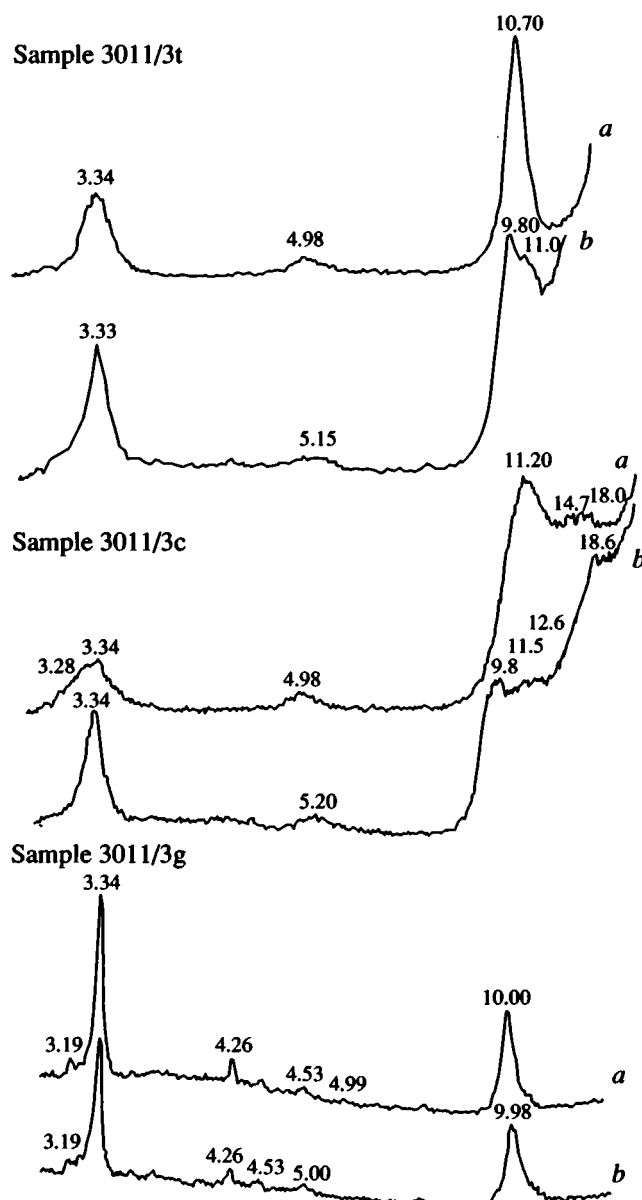


Fig. 5. Diffractograms of oriented preparations. (a) Natural state; (b) saturated with ethylene glycol.

($\text{Fe}_2\text{O}_3 + \text{FeO}$) content prevails over that of Al_2O_3 in all varieties (11.78–20.68 and 5.43–10.18%, respectively) and the K_2O content ranges from 5.17 to 8.99%.

Colloform mineral aggregates (Sample 3011/3c) are characterized by a lower content of main components and lower values of their sum (probably owing to elevated contents of volatile components), relative to the tabular mineral. Besides, they reveal a phase heterogeneity in X-ray image. Therefore, the reliable interpretation of data obtained for the colloform aggregates is hampered.

Chemical characteristics obtained for tabular and globular minerals support the diffraction data suggest-

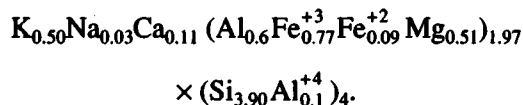
Chemical composition of authigenic minerals from lower Eocene sandstones of southern Dagestan, %

No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	K ₂ O	Na ₂ O	TiO ₂	H ₂ O ⁺	H ₂ O ⁻	Total
Tabular variety (Sample 3011/3t)												
1*	53.32	8.13	13.98	1.55	4.65	1.56	5.41	0.24	0.08	6.60	3.96	99.29
2	54.35	8.20	14.66		5.15	0.92	6.05	0.13	0.09	n. a.	n. a.	89.20
3	54.55	7.98	15.08		5.13	0.57	6.15	0.05	0.13	"	"	89.62
4	53.97	7.37	15.27		5.16	0.51	6.25	0.11	0.07	"	"	88.71
Colloform variety (Sample 3011/3c)												
5	51.41	9.30	11.78		4.91	0.58	5.17	0.09	0.08	"	"	83.37
6	49.66	8.91	12.67		4.70	0.71	5.29	0.21	0.06	"	"	82.22
Globular variety (Sample 3011/3g)												
7	51.23	10.18	16.72		4.03	0.36	7.31	0.09	0.11	"	"	90.03
8	51.56	9.50	17.76		4.30	0.65	7.59	n. d.	0.15	"	"	91.51
9	52.13	8.16	19.07		4.75	0.64	7.89	0.09	0.08	"	"	92.81
10	51.53	8.43	18.45		4.40	0.51	8.05	0.12	0.12	"	"	91.61
11	51.74	8.18	18.37		4.21	0.44	8.18	n. d.	0.14	"	"	91.26
12	51.25	7.12	20.68		4.26	0.53	8.53	0.04	0.08	"	"	92.49
13	51.63	7.22	20.55		4.52	0.44	8.54	n. d.	0.06	"	"	92.96
14	52.18	5.43	20.00		5.30	0.67	8.99	n. d.	0.09	"	"	92.66

* The silicate analysis of the sample was performed using the wet method; the sample also contains MnO (0.02%) and P₂O₅ (0.16%); CO₂ was not detected C_{org} = 0.25% (K.A. Stepanova, analyst). Other analyses were performed using the microprobe (Camebax) method (G.V. Karpova, analyst). (n. a.) Not analyzed, (n. d.) not detected.

ing that the Fe-rich dioctahedral 2:1 phyllosilicates represent the glauconite group minerals. However, the tabular glauconite bears some specific features.

In the tabular mineral (Sample 3011/3t), the SiO₂ content determined by both the silicate analysis (53.32%) and microprobe analysis (53.36–54.55%) methods is rather high (table). Using the silicate analysis data, as well as assuming that the whole SiO₂ is included in the mineral structure and the anion framework [O₁₀(OH)₂]⁻²² is constant, we obtained the following average crystallochemical formula:



It shows that the Si cation content is 3.90 f.u., which significantly exceeds the admissible limit for a typical glauconite. Therefore, the affiliation of the studied mineral to celadonite, which is characterized by a high degree of tetrahedral position occupation by Si (Si cation content is as much as 3.8–4.0 f.u., according to Drits and Kossovskaya, 1991), is necessary to discuss. Additionally, morphological and structural features of the mineral are most typical of celadonite rather than glauconite (Odin and Fullagar, 1988). Noteworthy is also a sufficiently high MgO content in the considered mineral (table).

Although quartz and mineral phases of amorphous silica were not revealed by the X-ray or electron

microscopy methods, the absence of quantitative chemical data on the free silica content hampers a reliable identification of the mineral composition based on the calculated crystallochemical formula. Therefore, percentages of mineral-forming oxides are used in further discussion.

The Fe/Al ratio in the studied mineral is more typical of glauconite rather than celadonite, because, according to (Buckley *et al.*, 1978; Odin *et al.*, 1988), the latter is usually characterized by higher Fe contents and lower Al contents (Fe₂O₃ + FeO and Al₂O₃ contents are 16–28 and 0.5–6.0%, respectively).

The noticeable K deficit (K₂O 5.41–6.25%) in the tabular mineral is probably related to the presence of swelling interlayers in its structure. This conclusion is consistent with diffraction patterns of the glauconite group minerals. In contrast, celadonites are usually characterized by higher K contents, e.g., the K₂O content is 7.69–9.89% (Buckley *et al.*, 1978) or 7.0–9.5% (Odin *et al.*, 1988). The formation of mixed-layer phases is also less typical of them, relative to glauconites.

In the opinion of Drits and Kossovskaya (1986, 1991), the *b* parameter of the elementary cell is not an unambiguous criterion for discrimination between glauconite and celadonite. Nonetheless, many researchers use this criterion accepting the value of *b* ≤ 9.06 Å for typical celadonites and *b* > 9.06 Å for typical glauconites (Kameneva *et al.*, 1981; Drits *et al.*, 1993).

As was noted, the b parameter of the tabular mineral is equal to 9.072 Å and more typical of glauconite, although this slightly elevated value is not prohibited for celadonite (Lipkina *et al.*, 1987; Drits *et al.*, 1993).

Taking into consideration the aforesaid, the studied dark green tabular mineral can probably be classed with glauconite, although elevated SiO_2 and MgO contents make it somewhat similar to celadonite as well.

Data on the chemical composition of globular glauconite (table, Sample 3011/3g) were obtained using the microprobe method. Therefore, we can compare the contents of main components in globular and tabular glauconites. Despite some heterogeneity of the chemical composition of globules with respect to the distribution of mainly Fe and Al contents and subordinate K, Si, and Mg contents (table), one can detect several substantial differences in the chemical composition of tabular and globular glauconites. For instance, as compared with the tabular variety, globules are characterized by higher K_2O and Fe_{tot} contents but lower SiO_2 and MgO contents, while the Al_2O_3 content is almost similar in both varieties (table).

On the whole, the chemical composition of dark green globular minerals in sandstones is rather typical of glauconites. This conclusion is also consistent with the data of Bunin (1968a, 1968b) on globular glauconites from lower Eocene rocks in southern Dagestan.

As compared with the globular variety, the tabular glauconite from fucoids is depleted in Fe but enriched in K and Mg. It shows a mixed-layer pattern (10–15% of swelling layers), which is probably responsible for lower K contents in the tabular mineral.

DISCUSSION

Paleocene–Eocene rocks of southern Dagestan are characterized by active processes of diagenetic mineral formation. At present, they are almost barren of organic matter, which was sufficiently abundant in fresh sediments and was buried along with numerous remains of calcareous and siliceous organisms. However, sedimentation environments in the region, e.g., relatively shallow-water settings, sediment reworking owing to unstable hydrodynamics suggested by the ubiquitous cross bedding, and bioturbation, promoted rapid decomposition of organic matter and the formation of slightly reductive conditions in sediments. Diagenetic processes and dissolution of foraminiferal tests produced a basal calcite cement in sandstones. Simultaneously, rare sulfide (pyrite) micronodules and globular glauconite grains (similar in size with the terrigenous material of host sediments) were formed. Inasmuch as oxidized varieties are absent amid glauconite globules, the glauconite reworking, which is suggested by its confinement to laminae of terrigenous material rather than biogenic mud, was probably subordinate and accompanied by an insignificant displacement of sediments.

Locally, for instance within the discussed biogenic structures, diagenetic processes were more intense than the background activity. Products of biological activity contained an elevated amount of organic matter. The central part of biogenic structures accumulated abundant excrements of Decapoda crustaceans enriched in C_{org} and P compounds. As a result of diagenetic processes, all these products were metasomatically replaced by silica to form a silicified lens with abundant sulfide mineralization, suggesting active sulfate-reducing processes in the area. Curved patterns of sandstone laminae, which envelop the silicified lens, suggest the lens formation during the early stage of diagenesis before the diagenetic consolidation of sediments and accumulation of basal calcite cement.

Burrows of Decapoda crustaceans in sandstones were not infilled with the host sediment. Their walls were covered by an organic substance produced by organisms during the movement in sediments (burrows are barren of coprolites). Pore waters of sandstones were enriched in many chemical components, particularly biogenic SiO_2 , which was produced as a result of the dissolution of diatoms and radiolaria, cations released during the metasomatic replacement of terrigenous feldspars with carbonates, and others. Organic matter in burrows favored the formation of specific diagenetic conditions, which were more reductive than the environment in enclosing sediments. The diffusion influx of substance from pore waters and local specific conditions promoted the formation of tabular and colloform Fe-phyllsilicates with a fine-dispersed pyrite admixture. During the diagenetic consolidation, burrows were crumpled and transformed into flattened bands. The diffusion influx of substances from enclosing sediments through burrow walls supplied a construction material for the newly forming minerals, first of all, into the contact zone of diagenetic silicates where the content of K and other cations is higher, relative to the mineral in central (axial) zones of burrows. Consequently, micaceous varieties were formed in the periphery of burrows, whereas the mineral with a noticeable share of mixed-layer phases was formed in the central zone with the lesser cation supply.

In sectors where relationships of globular and tabular minerals can be observed, it is seen that globular glauconite is enveloped by scales of the tabular variety (Fig. 3a); i.e., at first glance, it can be assumed that there is a significant difference in their formation time. Nonetheless, both of them represent products of diagenetic processes. The difference between them lies in the fact that the globular glauconite could be formed in several stages. After the formation in the upper sediment layer during the early diagenesis, the glauconite could be involved in reworking and, in this case, represent an allothigenic mineral. However, the reworking was insignificant and reworked sediments were practically deposited at the same site or only slightly displaced. As a result, sediments were differentiated into thin laminae mainly composed of terrigenous material with globular

glauconite and laminae with prevalent biogenic mud. The tabular glauconite, which was also formed during diagenesis in biogenic structures enclosed within sediments after the formation of globular glauconite, did not suffer subsequent reworking.

Shutov (1984) reported a joint occurrence of two generations of glauconite group minerals in the siliceous sandstone horizon of the Paleocene Yamnen Formation near Skole (eastern Carpathians). The minerals differ in geological position in the section and chemical composition. They are represented by the globular glauconite dispersed in sandstones and the skolite developed on walls of fucoids in the same sandstones. Unfortunately, this author provided no description and did not indicate morphological features of skolite aggregates. To explain formation conditions of these minerals, he proposed a model assuming the existence of a hydrothermal substance source common for both globular glauconite and skolite.

In our opinion, there is no need to look for sources of mineral-forming components other than bottom waters or diagenetic processes in accumulated sediments to explain the origin of authigenic phyllosilicates in sedimentary rocks of southern Dagestan.

CONCLUSION

(1) Biogenic structures are found in lower Eocene (Ipresian) rocks of southern Dagestan. Based on the unusual internal structure of coprolites confined to these burrows, it is assumed that the latter represent traces of Decapoda crustaceans.

(2) Burrows bear abundant authigenic mineralization. Coprolite accumulations in the central part of these structures are completely replaced by silica with abundant pyrite microinclusions. Burrows are filled with the newly formed, glauconite group minerals of two morphological varieties: tabular (mica-like) and colloform. They also differ in textural and chemical parameters: the tabular variety is enriched in silica, K, Mg, and Fe, relative to the colloform one, which is characterized by a larger share of mixed-layer phases. The globular glauconite from enclosing sediments contain more Fe and K but less SiO_2 , as compared with the varieties from burrows. Tabular, colloform, and globular glauconite varieties formed at early diagenetic stages. Differences between them are induced by specific features of geochemical conditions within sediments and biogenic structures.

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Some Specific Features of Early Vendian Sedimentation in the Southern and Middle Urals

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Abstract—The existence of the pre-Early Vendian hiatus in the Bashkir Meganticlinorium is supported by large incised valleys filled with Early Vendian sediments both on the western and eastern limbs of the meganticlinorium. It is suggested that a great glacioeustatic lowering of the sealevel occurred in the sedimentation basin. Taking into account the reconstruction of similar Early Vendian events for many provinces elsewhere, we can suppose that Early Vendian sedimentation basins in the southern and middle Urals were connected with the World Ocean. The comparative study of Lower Vendian sedimentary sequences in the Urals and Norway demonstrates similarities in rock associations. The correlation of Lower Vendian sections in the Urals with modern facies models of glacial sedimentation shows that glacial sequences of the southern Urals fit the shelf sedimentary associations proper. The character of section at the Serebryanka level in the middle Urals and the spatial distribution of mixtites therein correspond to sedimentation on the basin shelf and slope.

The Early Vendian history of sedimentation basins in the southern and middle Urals is as yet imperfectly reconstructed. In the 1960–1970s, the researchers mainly focussed their investigations on stratigraphy (Ablizin *et al.*, 1969; Gileva, 1985; Keller, 1966; Klyuzhina, 1991; Kukushkin, 1982; Mladshikh *et al.*, 1978; *Stratotip ...*, 1983; *Vendskaya ...*, 1985; *Verkh-nii ...*, 1982). Subsequently, the problem of Baikalian (Cadomian) folding was debated in several works (Alekseev, 1994, 1997; Alekseev and Alekseeva, 1988; *Formirovanie ...*, 1986; Ivanov, 1979, 1980, 1998; Puchkov, 1993, 1997a, 1997b, 1999; Rusin, 1998, 2000; Rusin and Krasnobaev, 1992). However, the evolution of Early Vendian sedimentation basins commonly remained beyond the scope of consideration. Publications by Aksenov (1998), Bekker (1968, 1988), and Chumakov (1978b, 1996) are only exceptions.

This work does not pretend to discuss all problems concerning Early Vendian sedimentary basins in the Urals. It only presents the first results obtained from the correlation of Lower Vendian sedimentary sequences in the southern and middle Urals with typical models of glacial associations. Some general features of the formation of Lower Vendian sedimentary sequences are also outlined. These data provide insights into the history of sedimentary basin formation on the western slope of the Urals 620–650 Ma ago. Isotopic constraints of the lower and upper limits of Early Vendian are given after Sokolov (1998).

LITHOSTRATIGRAPHY AND SEDIMENTATION CONDITIONS OF LOWER VENDIAN SEQUENCES IN THE SOUTHERN AND MIDDLE URALS

The Southern Urals

Figure 1 shows that Lower Vendian rocks are known both on the western limb of the Bashkir Meganticlinorium (Zilim River basin and near the Tolparovo Village) and on the eastern limb, extending from the Tirlyan Settlement in the north to the Starosubkhangulovo Village latitude in the south (Klyuzhina, 1991; Kozlov *et al.*, 1990; *Stratotip ...*, 1983; *Vendskaya sistema ...*, 1985). On the western limb, the Lower Vendian section is represented by the Tolparovo and Suirovo formations (Gorozhanin, 1988; Keller *et al.*, 1984; *Stratotip ...*, 1983). Previously, it was supposed that the Bakeevo Formation is also related to the Lower Vendian section on the western slope of the Bashkir Meganticlinorium (*Stratotip ...*, 1983). However, the isotopic dating of glauconite from silty sandstone of this formation (618 ± 13 Ma, based on the Rb–Sr isochron dating by Gorozhanin, 1995) indicates that this unit should most likely be referred to the base of the Upper Vendian section (Aksenov, 1998).

The Tolparovo Formation lies on eroded rocks of the Upper Riphean Karatau Group and is represented by yellowish gray or gray thick-platy sandstones with interlayers of mixtite, gritstone, conglomerate, and sparse argillite. Judging by angular limestone fragments and blocks from the Katav Formation, the pre-Early Vendian erosion affected deep levels of the Upper

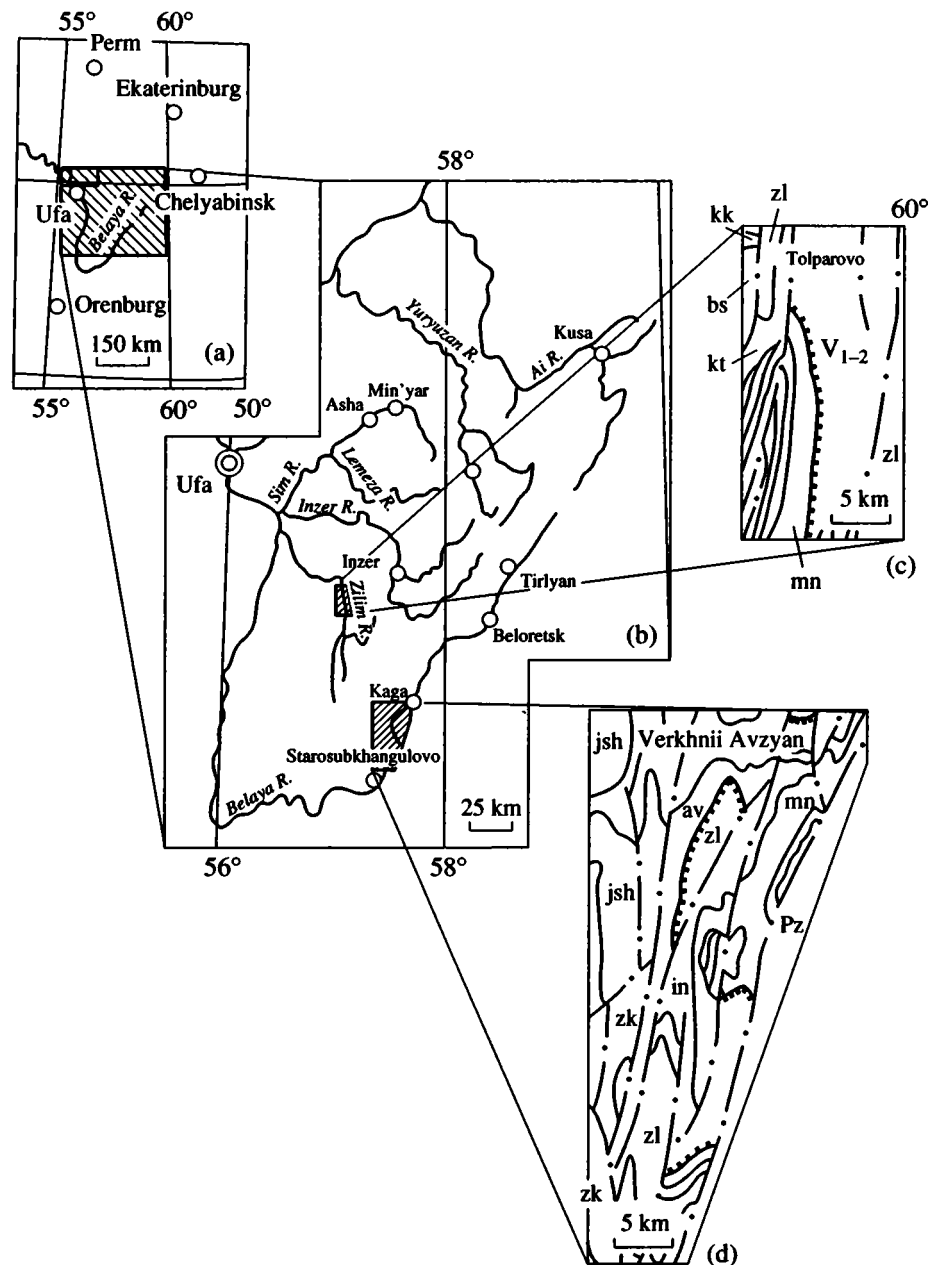


Fig. 1. (a, b) Index maps and schematic geological maps of the (c) vicinity of Tolparovo Village and (d) the Belaya River basin between Kaga and Starosubkhangelovo settlements on the western slope of the Bashkir Meganticlinorium.

Formations indices in (c) and (d): (jsh) Yusha, (zg) Zikal'ga, (zk) Zigaza-Komarovo, (av) Avzyan, (zl) Zil'merdak, (kt) Katav, (in) Inzer, (mn) Min'yar, (bs) Basu, (kk) Kukkarauk, (V₁₋₂) Lower and Upper Vendian rocks, unspecified.

Riphean sequence. The thickness of Tolparovo Formation reaches 600–650 m.

The Suirovo Formation, about 300 m thick, comprises siltstone and argillite with rare sandstone interlayers. Matrix-supported conglomerates are locally observed. According to Gorozhanin (1995), the model Rb–Sr age of the fine fraction (< 0.1 μm) of argillite from the Suirovo Formation is estimated at 638 ± 70 Ma. Rocks of the Suirovo Formation are conformably overlain by the Uryuk Formation. Based on geological data,

B.M. Keller (*Stratotip ...*, 1983) assumed that sedimentary rocks of the Tolparovo and Suirovo formations filled a large erosional valley, which was entrenched into Upper Riphean rocks. The entrenchment magnitude was estimated as more than 600–700 m (Keller *et al.*, 1984).

On the eastern slope of the meganticlinorium, Lower Vendian rocks are exposed in the Belaya River basin within the Krivolukskii Graben (Chumakov, 1978a, 1998; Klochikhin *et al.*, 1969; Kozlov, 1982;

Romanov *et al.*, 1982). Previously, sedimentary and volcanosedimentary rocks of the Arsha Formation from the Tirlyan and Arsha localities north of the Beloretsk area were also suggested to be members of the Lower Vendian section. However, the Rb–Sr isochron age of metavolcanics from the Arsha Formation turned out to be 677 ± 31 Ma (Gorozhanin, 1995, 1998). Therefore, rocks of the Arsha Formation probably belong to the uppermost Riphean. The Lower Vendian Kurgashlya Formation overlies various units of the Upper Riphean Krivolukskaya Formation with a clear erosional unconformity. The thickness of rocks eroded before the deposition of the Kurgashlya Formation was approximately 350–450 m (Chumakov, 1998).

The **Kurgashlya Formation** (160–200 m) comprises mixtites (several units, from 1–2 to 5–7 m thick) intercalating with packets of debris sandstone, along with massive and thin-bedded siltstone. In addition, the gritstone, small-pebble conglomerate, breccia, and dolomite sporadically occur in the lower part of the section. Varicolored quartz sandstone is prevalent in the middle part while thin-bedded gray shale and siltstone dominate in the upper part. Mixtite forms massive layers with sandy and silty matrix containing an admixture of clayey or clayey–carbonate material. The color of groundmass varies from lilac gray to gray or greenish gray. Fragments, 3–7 cm in size (occasionally up to 10 cm), are represented both by intra- and extrabasinal rocks (siltstone, limestone, metamorphic rocks, dolomite and its stromatolitic varieties, and quartz and arkose sandstones). Gabbroic fragments are also encountered. The composition and structure of mixtite and intercalating sedimentary rocks were reported in detail by Bekker (1968), Chumakov (1978a, 1978b, 1998), Klochikhin *et al.* (1969), Kozlov (1982), Romanov *et al.* (1980), and other investigators.

In addition to the mixtites, debris sandstones, along with their massive and rough lenticular (or irregular wavy) laminated varieties with numerous hieroglyphs at the base are among most typical lithotypes in the Kurgashlya Formation. In the 1950–1960s, all the above rocks were regarded as moraine formations (Lungersgausen, 1947, 1960). Bekker (1968) described them as tillite-type conglomerate.

The detailed study performed by Chumakov (1978a, 1978b, 1998, and others) revealed that mixtite layers are distal glacial marine deposits reworked by density flows. The debris sandstone including nonbedded varieties likely are also gravity sediments derived from mass and grain flows (Chumakov, 1998).

Rocks of the Kurgashlya Formation are linked with the overlying Bainazarovo Formation either by a gradual transition (Chumakov, 1998) or an erosion surface (Romanov *et al.*, 1980). The Bainazarovo Formation is represented by greenish gray quartzose or arkose (fine-, medium-, and coarse-grained) sandstones, siltstones, gritstones, small-pebble conglomerates, and shales. Klochikhin *et al.* (1969) correlated them with the

Uryuk Formation and the lower part of the Basu Formation. As is evident from Fig. 2, the same correlation is accepted in the modern stratigraphic schemes (*Stratigraficheskie ...*, 1993). The Kurgashlya Formation is correlated with the Bakeevo Formation. This suggests that sediments of the Kurgashlya Formation were deposited approximately in the interval of 605–630 Ma, i.e., in the latest Early Vendian. The correlation of the Kurgashlya mixtite with the Moelv tillite (Chumakov, 1998), which represents the second level of tillites in the stratotype section of the Lapland glaciohorizon, leads to the same conclusion. The isotopic age of the Moelv tillite is 612 ± 18 Ma (Sokolov, 1998).

Some Lower Vendian sections on the right bank of the Belaya River were studied in 1997 in cooperation with M.T. Krupenin from the Institute of Geology and Geochemistry, Ekaterinburg, and Ivo Palitz from the Technical University, Berlin. Previously unknown section in the large excavation along the new Kaga–Verkhniy Avzyan highway, approximately 1.5 km south of the Kaga Settlement, near the watershed dividing the Belaya and a Bol'shoi Avzyan rivers, turned out to be most interesting.

The eroded surface of stromatolitic dolomite of the Upper Riphean Min'yar Formation (thickness less than 20–25 m) is overlain by a mixtite bed. The latter is correlated with some mixtite layers of the Kurgashlya Formation in the Krivolukskii Graben located somewhat to the south. The thickness of mixtite bed is about 3 m on the northern wall of excavation and 1.2 m on the southern wall. In the latter case, the mixtite bed directly overlies the silicified dolomite of the Min'yar Formation. The uneven contact surface is bulbous. The dark, greenish brown matrix of the mixtite consists of clayey–silty material. Unsorted, poorly rounded fragments of quartzose sandstone, quartz veins, and carbonate rocks (size 2–3 mm to 1–2 cm) occupy up to 10–20 vol % and are practically lacking in the upper part of the mixtite bed. The mixtite is overlain by greenish and dark gray siltstone, about 0.5 m thick. Farther along the outcrop, one can observe coarse-crystalline massive and bedded dolomites with sparse lithic fragments of gravel dimension (12 m), thin-platey sandy dolomite with bioturbation signs and fucoids (4 m), and dark-gray brecciated and limonitized dolomite (3 m). These rocks are overlain by a siltstone and shale unit containing Upper Arenigian–Lower Llanvirnian graptolites (Erdtmann *et al.*, 1998).

The correlation of Upper Precambrian and Lower Paleozoic sections, which are known on the right coast of the Belaya River (Fig. 3), indicates that two important hiatuses exist on the eastern slope of the Bashkir Meganticlinorium. Immense volumes of Middle and Upper Riphean sedimentary rocks are inferred to be eroded during these hiatuses. The first (pre-Middle Ordovician) hiatus is known over more than 40 years (e.g., Krauze and Maslov, 1961). Based on the inferred average thickness of missing rocks and possible tec-

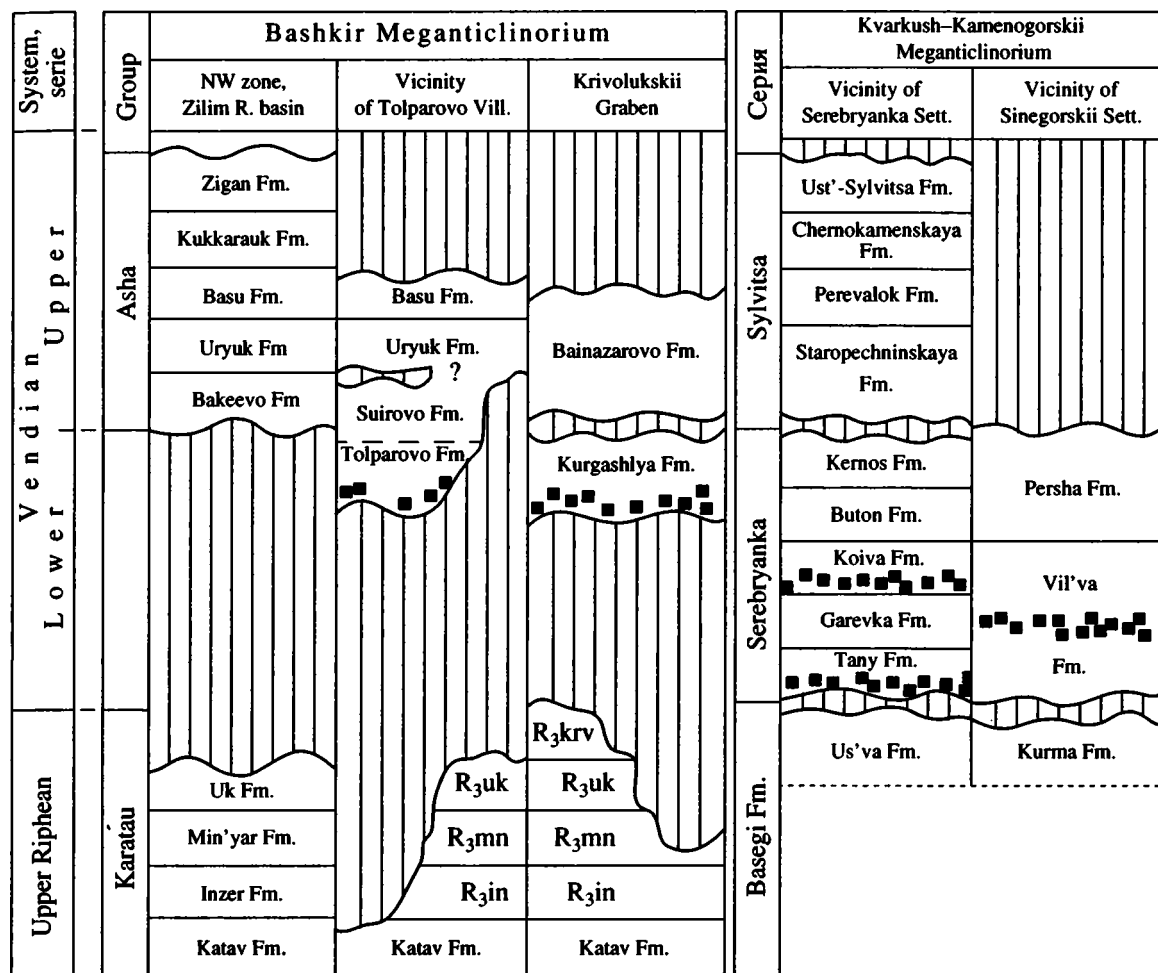


Fig. 2. Correlation scheme of Lower and Upper Vendian sedimentary sequences in the southern and middle Urals, based on (Chumakov, 1978a, 1978b, 1996, 1998; Keller *et al.*, 1984; Kozlov *et al.*, 1990; *Stratigraficheskie ...*, 1993, *Verkhniy ...*, 1982). Systems and divisions are adopted from (Sokolov, 1998). Mixtite levels are shown by filled boxes.

tonic overlapping, the related hiatus in some areas of the Bashkir Meganticlinorium is estimated at no less than 7–8 km. The maximal value can be 10–15 km or even more (Puchkov, 1997a).

In the section along the Kaga–Verkhniy Avzyan highway, the mixtite overlies not the uppermost Riphean formation (Krivolukskaya Formation), like within the Krivolukskii Graben, but substantially deeper units. Hence, the mixtite and associated massive sandstone, matrix-supported conglomerate, poorly sorted gritstone, and silty shale are relics of the sedimentary sequence, which filled a large erosional depression that was to some extent similar to the depression reported from the Tolparovo Village area on the western slope of the meganticlinorium. Thus, the late Precambrian history of the eastern slope of the Bashkir Meganticlinorium included a significant pre-Early Vendian hiatus marked by the formation of large incised valleys or canyons. Although their morphology remains ambiguous and is not as yet deciphered by geological and paleoge-

graphic maps, the correlation of sections on the right bank of the Belaya River casts no doubt for the existence of such valleys. However, it should be emphasized that the morphology of pre-Early Vendian downcuttings in the Tolparovo Village area is also so far unspecified.

The Middle Urals

In the Middle Urals, the Lower Vendian Serebryanka Group (Klyuzhina, 1991; *Stratigraficheskie ...*, 1993; *Vend'skaya ...*, 1985; *Verkhniy ...*, 1982) embraces the Tany, Garevka, Koiva, Buton, and Kernos formations.

The **Tany Formation** (360–800 m) is mainly represented by dark-colored mixtite, quartz–feldspar sandstone, and shale. Limestone and volcanics are subordinate.

The **Garevka Formation** (300–750 m) comprises the greenish gray and dark-colored, low-carbonaceous

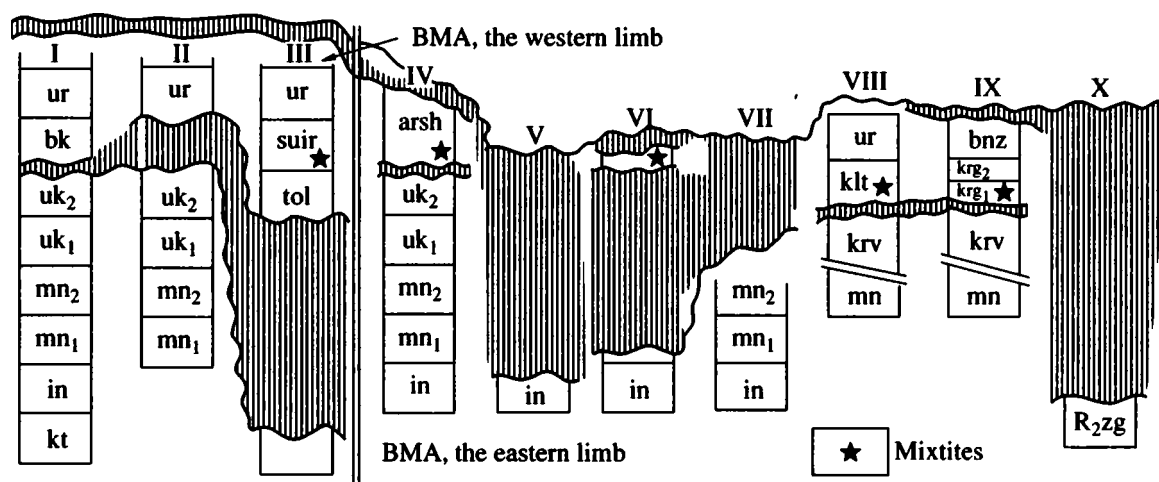


Fig. 3. Relationships between Late Riphean, Vendian, and Early Paleozoic sedimentary rock associations in sections of western and eastern limbs of the Bashkir Meganticlinorium (Maslov and Krupenin, 1998). (1) Tectonic contacts; (2) hiatus; (3) mixtite, tillite-like conglomerate, pebble stone. Sections: (I) mouth of the Saryshka River, Ust'-Katav, Zilim River near Bakeevo Village; (II) Basu River, Kulmas Settlement, Zilim River, Malyi Akkostyak Creek; (III) Zilim River, Tolparovo Village; (IV) Tirlyan Syncline; (V) Agidel Tourist Camp and Kaga Settlement proper; (VI) road cutting south of the Kaga Settlement; (VII) Belaya River near the Nizhniy Avzyan Village; (VIII) Belaya River near the mouth of the Apshak Creek; (IX) Belaya River upstream the Mindigulovo Village. Formations and subformations: (zg) Zigal'ga, (kt) Katav, (mn₁) Minka, (mn₂) B'yanka, (uk₁) Lower Uk, (uk₂) Upper Uk, (bk) Bakeevo, (ur) Uryuk, (tolp) Tolparovo, (suir) Suirovo, (arsh) Arsha, (krv) Krivolukskaya, (klt) Kal'tyagau, (krg) Kurgashlya, (bnz) Bainazarovo. (BMA) Bashkir Meganticlinorium; mixtite occurrences are shown by asterisks.

banded shales and quartz-feldspar sandstone. Rocks of the Tany and Garevka formations are intruded by granosyenite of the Troitsk Pluton. Based on the Rb-Sr isochron data obtained by A.A. Krasnobaev and Yu.L. Ronkin, the age of granosyenite is 621 ± 12 Ma (Kozlov *et al.*, 1990).

The **Koiva Formation** is represented by varicolored shale, silty shale, siltstone, limestone, dolomite, and dolomitized limestone. The thickness of the formation in the southern Kvarukh Meganticlinorium is about 250 m. Mixtite layers and volcanics appear in the northern section (Dvoretzskii Complex).

The **Buton Formation** (200–350 m) mainly consists of dark gray and black shales with fine-grained sandstone interlayers in the upper part of section.

The **Kernos Formation** (300–1500 m) is composed of quartz-feldspar and arkose rocks (sandstones and gritstones) and low-carbonaceous shales. Limestone and calcareous sandstone occur in a lesser amount. Slump structures, specific shale members with slump folds, and carbonate megabreccia units are typical of the upper Kernos Formation (Karta ..., 1983).

Mixtites from the Tany and Koiva formation were described in detail in (Chumakov, 1996; Klyuzhina, 1991; Kurbatskaya and Ablizin, 1970; and Verkhniy ..., 1982). At the Tany level, the mixtites commonly occur as homogeneous members, up to a few tens and hundreds of meters in thickness, composed of dark lilac or violet gray sandy-clayey rocks with differently rounded fragments varying in size from 1–2 cm to 3.5 m. Both intra- and extrabasinal rocks are observed among fragments. The extrabasinal fragments are rep-

resented by gneiss, granite, and granitic gneiss presumably derived from the Russian Platform basement (Chumakov, 1996; Kurbatskaya and Ablizin, 1970). Dropstones were noticed by Chumakov in thin-bedded shales at the top of the Tany Formation. Rhythmic sandy-silty-clayey members with gradational and fine cross-bedding, convolute (slump) deformations, erosion traces, and loading imprints at the base of sandstone interlayers were observed in the Tany Formation at the Mezhevaya Utkha River near the Tany Settlement.

Mixtites of the Koiva level are mainly red-colored and have a sandy-silty matrix. Fragments are represented by sedimentary rocks, granitoids, basic metavolcanics, and gabbrodiabase.

In the eastern Kvarukh-Kamennogorskii Meganticlinorium, rocks of the Tany and Koiva formations are replaced by sediments of the Vil'va Formation (*Stratigraficheskie ...*, 1993; *Verkhniy ...*, 1982). Mixtites are confined to the middle part of the section and distinguished from the western monotonous counterpart by an intercalation with banded shale and sandstone. A vague banding or bedding is occasionally noticed within the mixtites.

Carbonate units and layers, P₂O₅-rich thin-bedded shale, rock geochemistry, abundant slump and turbidite structures, etc. suggest that sedimentary rocks of the Serebryanka Group were deposited in a nearly linear marine basin with a rugged floor topography (Klyuzhina, 1991; Kurbatskaya and Ablizin, 1970; Mladshikh and Ablizin, 1967). Chumakov (1996) suggested that rocks of the Tany and upper Koiva formations match the glacial sediments in tectonically active

troughs, whereas rocks of the Garevka and lower Koiva formations were deposited during interglacial periods. Mixtites of the Vil'va Formation, which intercalate with thin-bedded shales, are distal formations, relative to the sections in the Serebryanka Settlement locality and presumably were formed on a submarine slope. Mixtites of the Tany Formation were accumulated in a submarine fan of thawed glacial water. The propagation of fan into the basin and the consequent mixtite accumulation were likely caused by a sealevel lowering.

SOME GENERAL FORMATION CONDITIONS OF LOWER VENDIAN SEDIMENTARY ROCKS IN THE SOUTHERN AND MIDDLE URALS

Viewpoints of researchers on the Early Vendian history of sedimentation basins in the southern and middle Urals remain controversial. In *Dokembriiskaya ...* (1988), for example, it was stated that the geosynclinal regime accompanied by oceanic crust formation started in Vendian–Cambrian, whereas the continental rifting was predominant in the Riphean. However, according to Khain and Bozhko (1988, p. 316), “the Vendian in the Urals was characterized by an activated rift regime and deposition of the sparagmite formation; by the end of the Early Vendian, aulagogens were closed and the sedimentation zone widened.” Parnachev (1986, 1988) also regarded Vendian sedimentary and volcanic complexes as specific graben rocks deposited in alluvial–proluvial and shallow-water marine environments under conditions of a relatively cold and humid climate. Klyuzhina (1991) also shared the similar ideas. She assumed that the Krivolukskaya and Kurgashlya formations were deposited under similar conditions within grabens, which originated after the erosion of underlying Upper Riphean rocks. Klyuzhina referred the Lower Vendian Serebryanka Group rocks to as the sparagmite sequence (Tany, Garevka, and Koiva formations) and the black shale sequence (Buton and Kernos formations, as well as some units of the Sylvitsa Formation). The sparagmite sequence includes continental and coastal-marine sediments, while the black shale sequence is represented by shallow-water sediments. Both sequences were deposited during the epoch of passive tectonic regime.

Characterizing Vendian igneous rocks on the western slope of the southern Urals, Alekseev (1994, p. 14) stated that “they were formed on the continental crust; therefore, magmatic associations of the initial stages of evolution are severely reduced or totally lacking.” Further, he noted that “in combination with other data, the above fact confirms the notion on evolution of the Urals during the Vendian geosynclinal–orogenic cycle.”

Puchkov (1999) characterized the Vendian geodynamics of the Urals as a time of tectonically quiet deposition of the shelf-type, shallow-water quartzite–shale and carbonate sequences, which “do not resemble the formations in active rifting zones.” On the contrary, according to data on the Vendian and Early Paleozoic

geodynamics of the Urals, “a series of riftogenic grabens and depressions filled with terrigenous and volcanosedimentary rocks” was developed throughout the Uralian Foldbelt during that time (Koroteev *et al.*, 1998). Necheukhin (1998) refers Vendian sequences in the Urals to as rock associations typical of the epicontinental rifting. Aksenov (1998, p. 79) points out that, in Early Vendian, the East European Platform occupied a rather high hypsometric position and underwent “an extraordinary evolution: vast territories were first covered by an ice sheet and then large trap basins started to evolve, indicating the onset of a drastic rearrangement of the structural framework.”

The modeling of glacial-marine sequence formation with the consideration of sedimentation and tectonic processes has shown that the retention of mixtite-bearing sequences and rock associations of other origins in geological records depends, first of all, on relationships between the tectonic subsidence and eustatic fluctuations of the sealevel (Brookfield, 1994; Eyels and Eyels, 1992; *Obstanovki ...*, 1990; and others). Glacial epochs differ from others by faster and more dramatic sealevel variations, which resulted in the formation of contrasting rock associations during the lowstand and highstand periods. During glacial periods at a low sealevel, the sedimentation is only confined to deep structures (rifts, continental slopes, and oceanic basins). Immature terrigenous sediments are prevalent in this case. Occasionally, they are supplemented by a carbonate clastic material supplied from eroded shelves. During interglacial periods and postglacial epochs, when the sealevel stands high, rather mature silicic clastic and carbonate sequences are formed. In the case of a relatively fast subsidence, sedimentation basins affected by glaciation are filled with thick sequences of glacial-marine clastic sediments alternating with interglacial sediments. The thickness of such sequences should be reduced upsection with decrease in subsidence rate.

To date, facies models of the glacial sedimentation have been developed rather well (Anderson and Molnia, 1989; Drodzikowski and Van Loon, 1991; Powell, 1984). Some of them were applied to Late Precambrian sedimentary associations (Brookfield, 1994; Fairchild, 1993). Several types of sedimentation sequences comprising rather a wide range of facies are typical for sedimentary basins in regions affected by glaciation (Fig. 4). In intracratonic environments (type 1), the isostatic uplift often hampers the stable deposition and retention of sediments. The formation of relatively thin glacial and interglacial sequences is possible here only under conditions of fast subsidence.

On shelves (type 2), during lowstand and slow subsidence, the continental ice can sporadically erode the older glacial and interglacial sediments. As a rule, only glacial deposits of the final stage and subsequent postglacial lithofacies are retained in such environment.

In narrow rift basins and on continental slopes (type 3), during lowstand, the thick sequences of glacial-marine

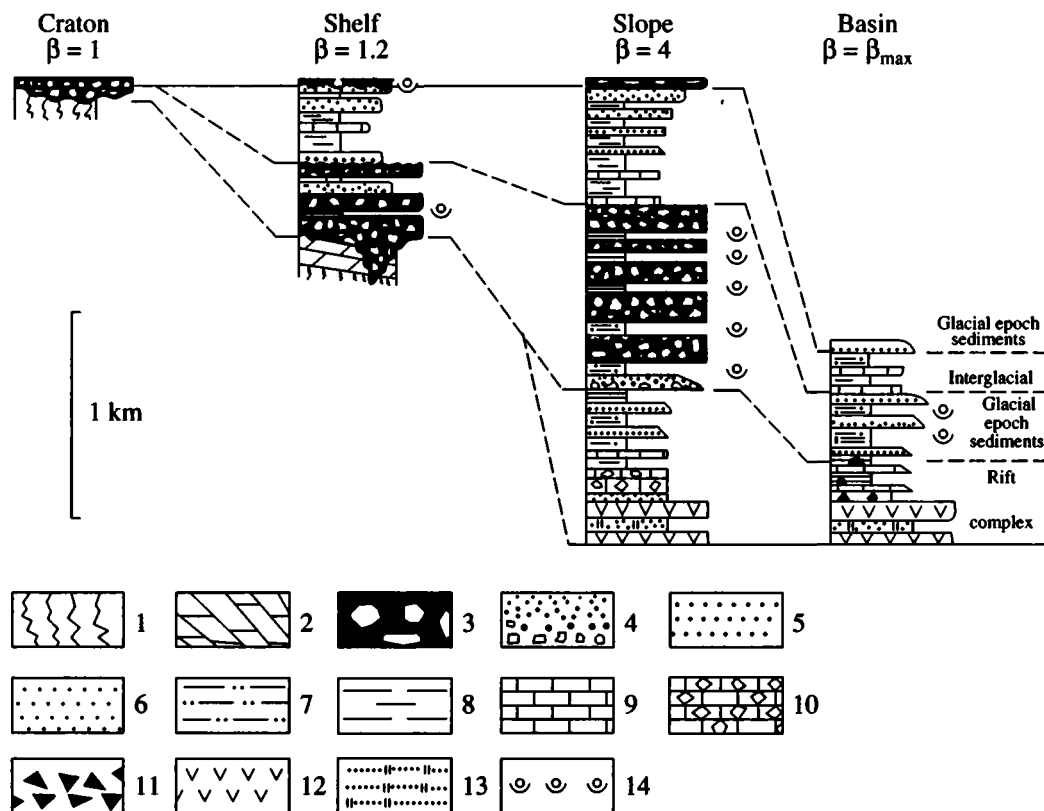


Fig. 4. Facies models of glacial sedimentation in craton, shelf, slope, and basin environments, based on (Brookfield, 1994). (1) Crystalline basement; (2) shelf carbonate association; (3) mixtite; (4) layers with a gradation bedding; (5) coarse-grained sandstone and gritstone; (6) fine- and medium-grained sandstones; (7) silty-clayey rock; (8) argillite and shale; (9) limestone; (10) brecciated limestone; (11) breccia unit; (12) basalt; (13) tuffaceous sandstone; (14) dropstone; β -values characterize an inferred factor of crust extension.

or glaciallacustrine sediments are formed. They are sharply or gradually replaced by fine-grained siliciclastic sediments and occasionally by carbonate sequences with upsection sealevel rising.

Sedimentary rock associations of type 4 are encountered in deep and wide rifts, marine basins, and oceanic deeps, where thin sections are only insignificantly affected by the adjoining land, the supply of immature siliciclastics from glacial areas, and eustatic fluctuations.

The above-listed types of glacialmarine sequences may also be outlined for Lower Vendian sedimentary rocks of the Urals. For example, in the southern Urals, relatively thin Kurgashlya and Tolparovo-Suirovo sequences, which contain mixtites mainly in lower parts of sections (Fig. 5, I and II), fill large erosion paleovalleys and are replaced upsection by coastal and shallow-water marine sediments. These sequences match type 2 glacialmarine rock associations on the shelf. The structure of sections at the Tany-Koiva level in the middle Urals and the spatial distribution of mixtites therein most likely correspond to the sedimentation style on shelves (western sections) and slopes (eastern sections) of the basin (Fig. 5, III and IV). This conclusion follows

from a substantial eastward increase in sediment thickness and a higher stratigraphic position of mixtites in eastern sections, relative to the western ones. The interfingering of thick and monotonous mixtite sequences, which are typical of the western sections, with packets and members of other lithotypes in sections of the Vil'va Formation furnishes an additional argument in favor of such inference.

Some difference in the Early Vendian sedimentation in the southern and middle Urals is outlined from the above reasoning. In the former case, it was most likely a zone corresponding to the craton-shelf system environment, where glacial and glacialmarine sediments were mainly retained in narrow incised (probably riftogenic) valleys and depressions. The available data do not bear certain indications on the possible westward or eastward direction of siliciclastic material transportation along such depressions. The shelf-slope model is more appropriate for the middle Urals, although the shelf dimensions were not likely to be great. If this was the case, the Early Vendian basin in the eastern Urals was opened to the east and, as will be shown below, probably connected with the World Ocean. This environment was fundamentally different from the Late

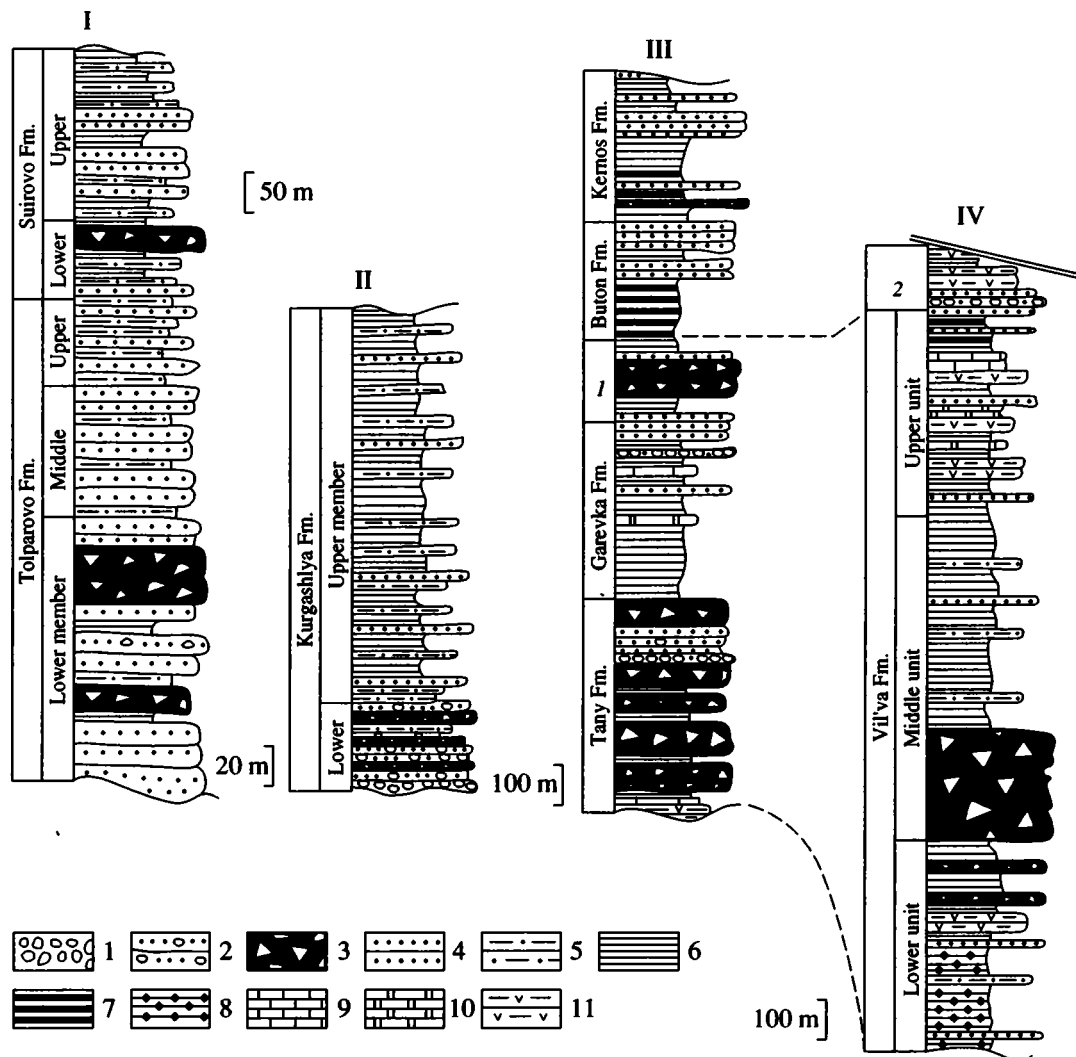


Fig. 5. Generalized Lower Vendian sections on the western slope of southern (I, II) and middle (III, IV) Urals, based on (Keller *et al.*, 1984; Kozlov, 1982; *Stratotip ...*, 1983; *Verkhniy ...*, 1982; and our data). Columns: (1) Koiva Formation, (2) Persha Formation. Sections: (I) Zilim River basin, the vicinity of Tolparovo Village; (II) Belaya River basin, district between the Bainazarovo and Muradymovo villages; (III) vicinity of the Serebryanka Settlement; (IV) southern termination of the Us'va-Sylvitsa Trough. (1) Conglomerate and gritstone; (2) matrix-supported conglomerate and sandstone; (3) mixtite; (4) sandstone; (5) siltstone; (6) argillite and shale; (7) low-carbonaceous shale; (8) magnetite shale; (9) limestone; (10) dolomite; (11) carbonate-chlorite-albite and albite-chlorite schists (metavolcanics).

Vendian sedimentation basin where the siliciclastic material was transported both from the west and east (Bekker, 1968 and others).

with early Vendian sedimentary rock associations on the western slope of the Urals.

EARLY VENDIAN SEDIMENTARY ROCK ASSOCIATIONS IN THE URALS AND NORWAY: DATA FOR A COMPARATIVE OVERVIEW

Lower Vendian sequences in Norway are presently best studied with respect to sedimentology (Banks, 1973; Chumakov, 1978b; Dreyer, 1988; Edwards, 1984; Nustien, 1982; Sokolov, 1998). Therefore, they have been chosen for the sedimentological correlation

Northern Norway

In Finnmark, northern Norway, the Vestertana Group includes the Smalfjord, Nyborg, and Mortensnes formations that cover the age interval of 620–650 Ma (Edwards, 1984; Siedlecka and Roberts, 1992; Sokolov, 1988; Vidal and Moczydlowska, 1995).

The **Smalfjord Formation**, from a few meters to 50 m thick, comprises gray-colored diamictites, which overlie the eroded surface of the Tanafjord and Vadsö groups rocks, and medium-platy, massive or vaguely

banded sandstones. Two lithofacies types are identified in the section. Type 1 lithofacies, which comprises sandstones with interlayers and lenses of conglomerate, fills up a series of paleovalleys (Varanger, Krokvan, and others). It was formed from gravity flows and attendant fluvial sediments in a multichannel river system. In the Krokvan paleovalley, sandstones of the Smalfjord Formation are incised in underlying rocks for a few hundreds of meters, and the total thickness of older rocks, which were eroded before the deposition of basal beds of the Smalfjord Formation, is estimated at more than 2000 m (Edwards, 1984). Type 2 lithofacies, which consists of tillites with argillite interlayers, represents a glacial, fluvioglacial, or periglacial formation (Siedlecka and Roberts, 1992).

The **Nyborg Formation**, about 300 m thick, comprises varicolored (or light gray) dolomites and shales intercalating with brick-red, greenish, or light gray sandstones with a horizontal, wavy, or graded lamination and massive structure. The Nyborg Formation overlies the older rocks with a small hiatus and, in turn, is unconformably overlain by the Mortensnes tillite. The Nyborg Formation was deposited over several stages. The fast initial transgression was successively followed by the relatively quiet sedimentation, fan degradation and progradation at flanks of the basin, regression, and shallow-water sedimentation (Siedlecka and Roberts, 1992; Vidal and Moczydlowska, 1995). The Rb–Sr whole-rock isochron age of argillite from the Nyborg Formation is estimated at 654 ± 7 Ma (Roberts *et al.*, 1998).

The **Mortensnes Formation** (0–50 m) mainly consists of tillite with a subordinate amount of shale, thin- and thick-platy, poorly sorted and graded sandstone, conglomerate, and dolomite.

Southern Norway

In the Hedmark Basin of southern Norway, the Lower Vendian Hedmark Group includes the Osdalen (Rendalen, Ring, etc.) and Moelv formations (Kumpulainen and Nystien, 1985; Sattler and Nystien, 1981; Nystien, 1982; Sokolov, 1998; Vidal and Moczydlowska, 1995). Rocks of the Ekre Formation overlying the Moelv Formation have an isotopic age of 612 ± 18 Ma, and, therefore, apparently belong to the Upper Vendian.

The **Osdalen Formation** is represented by shale, thin-bedded turbidite sandstone, coarse arkose, and massive or graded conglomerate forming several intrabasinal fans. In the mid-1970s, it was suggested that these rocks are related to the deltaic facies. Subsequently, they were referred to as gravity sediments. The basal breccia, clast-supported conglomerate with sandstone and argillite interlayers, and matrix-supported conglomerate are recognized as specific lithofacies. The basal breccia was formed in the environment of multichannel alluvial plain entrenched into underlying

mud–carbonate sediments of a tidal plain. The depth of incised valleys is estimated at 300–350 m (Nystien, 1982). The clast-supported conglomerate, which is observed as continuous layers (0.5–5.0 m thick) along the strike, is marked by a rough horizontal stratification and graded bedding. This lithofacies was formed during the migration of longitudinal sandy and pebble bars in wide channels, or large-scale floods. The matrix-supported conglomerate occupies up to 70–80% of the total Osdalen Formation thickness. This is a nonstratified, poorly sorted rock probably formed from subaerial clastic flows (Nystien, 1982).

The **Moelv Formation** lies with an erosional unconformity over older rocks. Locally, it unconformably overlies not only the Osdalen Formation but also the Upper Riphean Etna quartzite. The clast-supported mixtite is the prevalent lithofacies, which is considered to be a basal till of the land glacier (Sattler and Nystien, 1981). Fluvioglacial and probably lacustrine-glacial conglomerates, fine-grained sandstone of the turbidite origin, and fine-eliminated argillite with dropstones are associated with the mixtite. The thickness of the Moelv Formation varies from 2 to 20 m. Upward the section, the tillite is gradually replaced by glacial-marine shale with dropstones.

The evolution of the Hedmark Basin in the late Riphean and Early Vendian is comparable with the evolution of the majority of other sedimentary basins on the western margin of Baltoscandia (Siedlecka and Roberts, 1992; Vidal and Moczydlowska, 1995). Their origination was related to early phases of the Yapetus ocean opening. Up to the Varanger glaciation, they were represented by relatively deep, marine troughs with turbidite sedimentation in the center and alluvial deposition at the periphery. Previously, it was assumed that the basin regression, alluvial fan formation, and intense gravity sedimentation were related to a transitional phase of tectonic activity in the time when the Osdalen conglomerate was formed (Nystien, 1982). However, a glacioeustatic sealevel fall is inferred recently.

General sedimentological features and formation conditions of Lower Vendian sedimentary rocks of Norway are summarized in Table 1. The similar information on Lower Vendian rocks in the Urals is given in Table 2 for comparative purposes. Based on these data, some more or less common features of the formation of Early Vendian sedimentary rock associations may be outlined both for the Urals and Norway.

Specific features of mixtite-bearing units. Early Vendian mixtite-bearing units are characterized by the predominance of sediments of the mass, grain, and other types of gravity flows, as well as fluvio-, limno-, and periglacial sediments represented by mixtites, debris sandstones, and their graded and massive varieties containing siltstone, dolomite, and shale interlayers. The relationships with underlying rocks are surprisingly similar in most of the above cases: the deep ero-

Table 1. Some general features of Lower Vendian sedimentary sequences in the northern and southern Norway

Specific features of mixtite-bearing units and correlative rocks				Specific features of rocks overlying and intercalating with mixtite units		
Rocks	Genesis of sedimentary rocks	Relationships with underlying rocks	Relationships with overlying rocks	Rocks	Genesis of sedimentary rocks	Relationships with overlying rocks
Northern Norway						
Diamictites and sandstones with conglomerate lenses; poorly sorted, massive and gradation-bedded sandstones, dolomites, and shales	Gravity flows and fluvial deposits; glacial proper, fluvioglacial, and periglacial deposits	Deep (up to hundreds and a few thousands of meters) erosion of underlying rocks with the formation of incised valleys	Rocks overlie the mixtite-bearing units with an erosion at the base	Dolomites and red- or varicolored shales; stromatolitic dolomites	Sediments of tidal platforms; sedimentation under conditions of fast transgression; quiet sedimentation, progradation of fans, and shallow-water marine sedimentation in successive zones	Unconformable overlying
Southern Norway*						
Clast-supported mixtites, conglomerates, sandstones, and argillites	Subaerial tills; fluvioglacial and lacustrine-glacial deposits	Incised valleys with a magnitude of a few hundreds of meters	Gradual transition to glaciomarine shales with dropstones	Shales, coarse-grained sandstones, and massive or gradation-bedded conglomerates	Mainly gravity deposits formed in frontal zones of deltaic belts in combination with sediments of multichannel alluvial valleys, pebble bars, and subaerial clastic flows	Deposits gradually replaced upsection by glaciomarine sediments with dropstones

* General features of sedimentation: regression of the basin, development of alluvial fan system triggered by a sharp lowering of sealevel, and drastic intensification of gravity sedimentation.

Table 2. Some general features of Lower Vendian sedimentary sequences in the southern and middle Urals

Specific features of mixtite-bearing units and correlative rocks				Specific features of rocks overlying the and intercalating with mixtite units		
Rocks	Genesis of sedimentary rocks	Relationships with underlying rocks	Relationships with overlying rocks	Rocks	Genesis of sedimentary rocks	Relationships with overlying rocks
Southern Urals						
Gray and dark-colored mixtites, debris sandstones, siltstones, and shales	Deposits of various (mass, grained, etc.) gravity flows are predominant	Unconformity and erosion down to 400–700 m. Large incised valleys are present	Gradual transition to the coastal and shallow-water marine sediments	Massive sandstones without bedding, sandstones with rough lenticular or irregular wavy bedding, hieroglyphs at the base, varicolored quartz sandstones, and thin-bedded siltstones and argillites	Shallow-water marine and gravity deposits	Slight erosion
Middle Urals						
Lilac-gray and red mixtites with silty-clayey or sandy-silty matrix; shales	Mainly marine deposits related to the turbidite flows, slumping of semiconsolidated sediments and related processes, along with the thawing out of moraine material from the shelf glacier	Slight erosion of underlying rocks	Deposits are overlain with an erosion at the base by coastal and shallow-water marine sediments	Greenish gray to gray shales and low-carbonaceous shales, sandstones, limestones, volcanics, limestones, and dolomites in some sections	Mainly shallow-water marine deposits	Gradual transition to shallow-water marine sedimentary rock associations

sion with a magnitude of hundreds of meters and the existence of large incised valleys and channels at the base. Upsection, the mixtite-bearing units are either gradually replaced by shallow-water marine sediments or overlain by the same rocks with an insignificant erosion.

Specific features of rocks overlying or intercalating with the mixtites. Mixtite units are commonly alternating with perilittoral, shallow-water marine, and moderately deep-water sediments, such as shales, dolomites, packets and members of intercalating argillites, siltstones, and fine-grained sandstones or gravity deposits formed within the frontal zones of deltaic belts in association with sediments of the multichannel alluvial plains, pebble bars, and subaerial clastic flows. The latter are represented by the massive sandstone without bedding or the sandstone with a rough lenticular (or irregular wavy) bedding and numerous hieroglyphs, as well as by members of intercalating sandstones, siltstones, and argillites. In some cases, carbonate sediments of tidal platforms also occur.

General features of the sedimentary sequence formation. As can be deduced from the aforesaid, the most general formation conditions of the sedimentary sequences under consideration include the regression of sedimentation basin induced by glacioeustatic events, the deposition of an enormous volume of gravity deposits, and the formation of large, deeply entrenched valleys and canyons.

Hence, it may be inferred that, on the eastern margin of the East European Platform (southern and middle Urals) and its northwestern margin (southern and northern Norway), Lower Vendian sedimentary sequences demonstrate a great glacio-eustatic fall of the sealevel. Indications on such event were also noticed in some other regions. The Wonoka canyons in the Adelaide Geosyncline are the most attractive example of such event (Christie-Blick *et al.*, 1990; DiBona and Von der Borch, 1993; Lindsay, 1989; Von der Borch *et al.*, 1988). Thus, all the above-mentioned basins were connected with the World Ocean. For the Urals, this inference most likely implies that an Early Vendian shallow-water shelf basin or several basins existed in the west within the present-day paleocontinental sector, whereas the ocean was situated to the east, including northern sectors of the present-day Central Urals Zone, probably the Timan-Pechora, and other regions. This suggestion is consistent with recent paleogeodynamic reconstructions (Dushin, 1997). In Late Vendian, the paleogeographic situation was drastically changed. The eastern and presumably central regions of the present-day Urals, which were transformed into an area of vigorous erosion, served as a main provenance of coarse siliciclastic material supplied into the region of the western slope.

CONCLUSION

The data presented above lead to the following conclusions. First, the pre-Early Vendian hiatus existed in the Bashkir Meganticlinorium and an immense volume of Upper Riphean sedimentary rocks was eroded at that time. Previously, this assertion was based on the fact that a valley with the magnitude of entrenchment up to 600–700 m was outlined by Keller, Veis, and Gorozhanin within the Zilim River basin on the western slope of the Bashkir Meganticlinorium. The valley was filled with Lower Vendian sediments and incised into Upper Riphean rocks of the Karatau Group. At present, these notions have been confirmed by the data on geology of Upper Riphean and Vendian sedimentary sequences on the eastern limb of the meganticlinorium. The deposition of Lower Vendian sediments and the prevalence of gravity sediments in large, deeply entrenched valleys and canyons in the southern Urals suggest that the sealevel in Early Vendian sedimentation basin sharply lowered due to the glacioeustatic processes. Similar Early Vendian events have been reported from many regions all over the world. Taking into account the fact that these events were contemporaneous, it may be suggested that Early Vendian basins in the southern and middle Urals were connected with the World Ocean.

The correlation of Lower Vendian sedimentary sequences in the southern and middle Urals with counterparts in Norway revealed some similarities in rock associations. For example, the deposits of various gravity flows, as well as peri-, fluvio- and lacustrine-glacial sediments are typical of mixtite-bearing units. These sediments generally overlie the older rocks with a deep erosional unconformity and fill large incised valleys and channels. The replacement of mixtites upward the section by shallow-water marine sediments is either gradual or noted by a slight erosion. Mixtite units also alternate with perilittoral and shallow-water marine sediments, which were formed in frontal zones of deltaic belts. Thin carbonate units of the tidal origin are sporadically present.

The correlation of Lower Vendian sections in the Urals with modern facies models of glacial sedimentation has shown that the relatively thin glacial sedimentary sequences of the southern Urals, which include mixtites in the lower parts of sections, match rather well sedimentary associations of the shelf proper. The structure of sections at the Serebryanka level in the middle Urals and the spatial distribution of mixtites therein correspond to the sedimentation on the shelf (western sections) and slope (eastern sections) of the sedimentary basin. The aforesaid points to some differences in Early Vendian sedimentation in the southern and middle Urals. In the former case, it most likely was a zone, which fitted the cratonic shelf environment with an active reworking of previously deposited glacial and glacialmarine sediments and their retention in deep entrenched valleys. The basin in the middle Urals matches the shelf slope model. However, in both cases,

the general paleogeographic situation in the Early Vendian was drastically distinct from the Late Vendian time when intra-Uralian provenances became also important in the delivery of materials to sedimentation basins as a result of the Cadomian (?) orogeny.

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Epigenesis of Middle Riphean Rocks in the Bashkir Meganticlinorium, Southern Urals: Timing of Alterations and Geological Implications

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Abstract—The Rb–Sr and K–Ar characteristics of whole-rock argillite samples from the Middle Riphean Yurmatinian Group have been studied. The timing of final rock alteration was estimated at 525 ± 30 Ma by the Rb–Sr geochronometer. In the section near the Bol'shoi Avzhyan Settlement, the rocks experienced alteration up to the stage of deep epigenesis. The K–Ar data indicate that rock alterations continued after the Rb–Sr system conservation and was accompanied by a gradual gain of K. The great temporal gap between alterations of Middle and Lower Riphean rocks was established in the southern Urals. This gap may be explained either by the affiliation of sampled rocks to different tectonic units or by principal errors in stratigraphic correlations.

INTRODUCTION

The Bashkir Meganticlinorium in the southern Urals is a vast region where Upper Precambrian sub-platform rocks are exposed over an area of 110×350 km and overlain by folded Paleozoic sequences in the north, east, and west. The meganticlinorium is a tectonic unit of the Central Uralian Uplift. It is bordered with the West Uralian outer fold zone in the west, the Uraltau Anticlinorium in the east, and the Zilair Synclinorium in the southeast (Sobolev *et al.*, 1986).

In terms of the character of folding and structure of ancient sequences, along with magmatism and metamorphism in the region, the Bashkir Meganticlinorium is subdivided into the western and eastern zones. The western section (total thickness of >10 km) comprises the Burzyanian, Yurmatinian, and Karatavian groups. This section is the stratotype of the Riphean, which is the main unit of general chronostratigraphic scale of the Upper Precambrian. The above groups are regarded as typical sedimentary complexes of synonymous erathems (Semikhatov *et al.*, 1991).

In most overviews on the Riphean of the Bashkir Meganticlinorium, it is emphasized that the above-mentioned three groups correspond to sedimentary megacycles and are separated from each other by hiatuses and angular unconformities. Indications of ancient weathering have been found beneath the bases of Yurmatinian and Karatavian groups (Stratotip ..., 1983). Most controversies are related to the Yurmatinian–Karatavian transition. To date, three interpretations are competing: (1) both groups are linked by a gradual transition, at least in some localities (Kozlov *et al.*, 1997); (2) both groups are everywhere separated by an

unconformity (Maslov, 1997); (3) the Kuzha Group locally wedges in between Yurmatinian and Karatavian groups (Filippov, 1997).

In contrast to traditional notions on the structure of Riphean stratotype in the southern Urals with its subdivision into three discrete groups, the new views on tectonically thrice-repeated section became rather popular in recent years (Ivanov and Ivanov, 1997). Such notions, which deny the Riphean as a general subdivision of Precambrian, were also proposed by Kamaletdinov (1974, 1977).

The interpretation, which supposes a regular lateral juxtaposition of the Burzyanian, Yurmatinian, and Karatavian groups, is consistent neither with indications of erosion at the base nor with specific lithological features of each group (Maslov, 1997). For example, thick sequences of substantially carbonaceous argillites intercalating with sandstones and siltstones, along with the marked predominance of chemogenic dolomite in the middle part of the section, are particularly typical of the Lower Riphean Burzyanian Group. Characteristic sequences of conglomerates and sandstones associated with basic and less frequent acid volcanics are known from the lower part of the Yurmatinian Group and are especially abundant on the eastern limb of the Bashkir Meganticlinorium. Upsection, they give way to quartz sandstones, siltstones, argillites, and complex polyfacies terrigenous–carbonate sequences.

The Upper Riphean Karatavian Group is characterized by different rock types. The section begins with a thick complex of arkose sandstones, which are related to volcanic rocks, gritstones, and siltstones. Upsection, they give way to varicolored carbonate rocks, sand-

stones, siltstones, argillites, reefogenic (stromatolitic and microphytolitic) dolomites, and limestones.

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It was assumed that problem of correlation could be solved by means of the isotope dating of sedimentary rocks, and a great deal of such investigations were carried out. Unfortunately, stratigraphic implications of these works are scanty, because the dating of rocks is hampered or becomes impossible owing to several factors. In particular, the isotopic systems are distorted due to the secondary (epigenetic) alteration of rocks, and the measured age has no relation to the sedimentation time. Therefore, the isotopic dating of sedimentation, especially Precambrian, should only be based on the age determinations for igneous rocks. The search for relevant rocks of this kind is by no means a simple problem.

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Experimental data points may be somewhat scattered relative to the straight line, due to analytical errors or natural noise, i.e., not exact fulfillment of conditions required for isochron dating (incomplete closure of the system and different times of rock formation or transformation. If analytical errors dominate, the straight line is called isochron. If the natural noise is prevalent, it is defined as errochron.

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Rb–Sr dating of sedimentary rocks. Authigenic clay minerals commonly attract the main attention in the dating of sedimentary rocks. If the authigenic mineral is formed in equilibrium with seawater, the Sr isotopic composition in minerals is controlled by the Sr signature of seawater and hence turns out to be the same in all authigenic materials. Thus, the initial condition for the isochron method application is satisfied. However, the actual situation is much more complicated. First, the time of authigenic mineral formation is uncertain and may substantially depart from the time of sedimentation. Second, precisely authigenic minerals most readily undergo secondary alterations, and isotopic systems therein are distorted. All this severely limits the possibility of dating.

As is known, the main mass of sediments is of terrigenous origin; therefore, for a long time, the dating of clastic rocks seemed to make no sense. Nevertheless, such attempts were repeatedly undertaken and based on the following idea. During the deposition of sediments, which are products of the destruction of various rocks in provenances, the sediments are mechanically mixed, and their composition is averaged. First of all, this is related to fine sediments of clay and silt dimensions. It may be assumed that the Sr isotopic composition also undergoes the averaging, so that a certain volume of whole-rock sample with the same isotopic composition may be selected. Therefore, if the secondary alteration of fine sediments is eliminated, the whole-rock samples could be used for the timing of sedimentation.

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Table 1. Rb–Sr characteristics of argillites in the Bashkir Meganticlinorium of the southern Urals

Sample no.		$\mu\text{g/g}$		$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
lab	field	Rb	Sr		
Yusha Formation (R_1)					
4525	A-39	172	52.24	9.64	0.86731
4526	A-40	156	84.53	5.39	0.81888
4527*	A-41	99.5	62.78	4.62	0.79665
4530*	A-44	226	105.0	6.32	0.83828
4532	A-46	155	106.8	4.24	0.80183
4533	A-47	158	20.76	22.7	1.04850
Mashak Formation					
4524	A-38	155	27.27	16.8	0.92857
Zigaza–Komarovo Formation					
4473	A-48	192	39.05	14.5	0.90433
4475	A-50	203	28.01	21.5	0.95702
4476	A-51	225	25.37	26.4	0.99743
4545	967/7	207	33.58	18.3	0.93412
4548*	967/10	164	36.86	13.2	0.90598
Avzyan Formation, Kataskin Subformation					
4477*	A-59	209	11.14	57.1	1.23886
4478*	A-60	229	8.829	80.5	1.42815
4479*	A-61	208	13.29	47.3	1.13591
4480	A-63	255	11.14	70.0	1.30071
4481	A-65	260	11.08	72.0	1.30115
4482	A-67	243	11.13	66.4	1.24598
4483	A-69	236	12.16	58.9	1.18900
4485	A-71	63.3	26.20	7.06	0.81328
4486	A-72	274	6.803	128	1.73260
4492	A-84	200	16.89	35.3	1.01572
4493	A-86	211	29.85	30.0	0.97616
Avzyan Formation, Malyi Inzer Subformation					
4497	A-1	251	20.09	38.0	1.03587
4498	A-2	129	25.68	14.8	0.84166
4499	A-3	164	13.16	37.3	1.05068
4500	A-4	196	15.7	37.2	1.03300
4494	A-88	256	14.23	54.5	1.18514
4495	A-89	55.0	40.98	3.91	0.76030
4496	A-91	219	14.09	46.6	1.09105
Avzyan Formation, Kutkur Subformation					
4502	A-27	183	18.10	30.1	0.99764
4504	A-29	201	15.36	39.25	1.08213
4505*	A-30	142	15.84	26.9	1.08434
4506	A-31	183	18.10	28.7	1.00586
4507*	A-32	163	13.42	36.2	1.03158
4509	A-34	193	13.35	43.4	1.10599
Avzyan Subformation, Revet Subformation					
4516	A-8	165	24.86	19.6	0.92734
4512	A-21	102	23.76	12.7	0.87110
4513	A-23	180	9.8	55.9	1.21155
4514	A-25	146	31.48	13.7	0.88280
Kuzha Group					
4550	Hole113	124	33.36	11.0	0.88665
4551	Hole111	204	20.67	29.7	1.11108
4552	Hole111	229	20.78	33.2	1.13390
4553	Hole18	167	60.81	8.08	0.84461
4554*	Hole254	207	75.74	7.99	0.81554

* Samples omitted from age calculations.

Riphean Mashak Formation. The Yusha and Mashak sedimentary rocks occur in the Yamantau Anticlinorium within the axial part of the Bashkir Meganticlinorium, i.e., 150–200 km south of the Burzyanian strato-type locality. Results of Rb–Sr datings are given in Tables 1 and 2. Age calculations for the new series of samples from the uppermost Lower Riphean yielded values on the order of 908 ± 73 Ma, which are the value close to the values previously obtained for the strato-type section. Such coincidences are difficult to explain by accidental causes. Therefore, we assume that the age of epigenetic alterations of Lower Riphean rocks in the Bashkir Meganticlinorium previously estimated at 930 ± 40 Ma actually reflects a real event.

We think that mechanisms of the averaging of Sr isotopic composition in large volumes of sedimentary rocks are still rather ambiguous and require additional studies. Strontium, a chemical analogue of Ca, is mainly included in plagioclases of terrigenous rocks. In clay, Sr is rarely incorporated into the structure of phyllosilicates and commonly adsorbed at the surface and within the interlayer space of clay particles. Since, the averaging is related to Sr originated from the Rb decay, the complete recrystallization of material is needed for its release and isotopic homogenization. Hence, the given stage of epigenetic alterations was accompanied by a severe modification of rock composition.

Detailed mineralogical studies (Anfimov, 1997; Kagarmanova, 1998; Maslov *et al.*, 1999) and our own observations have shown that Riphean sediments of the Bashkir Meganticlinorium underwent the stage of deep epigenesis and initial metagenesis with extensively developed secondary potassic feldspathization, muscovitization, and other processes. It is evident that such intense transformation could occur only under the impact of water solutions. The influence of such solutions was the factor that was responsible for the averaging of Sr isotopic composition in large rock massifs.

Burzyanian rocks underwent metagenetic alterations and, in some cases, bear indications of an incomplete metamorphism (biotite facies). The authigenic biotite, chlorite, quartz, and potassic feldspar assemblage is observed in various parts of the Ai Formation. It is ubiquitous in the Kisezan Subformation and widespread in the Lower Kusa and Polovinkino subformations of the Satka Formation.

The Yusha Formation at the roof of the Burzyanian Sequence attracts the particular interest. Rocks of this formation are represented by a fine intercalation of argillites, siltstones, and fine-grained sandstones. Alterations in rock samples from the Yusha Formation are not stronger than the stage of deep epigenesis. In all rocks, the biotite-series micas are replaced by packets of chlorite–vermiculite and chlorite–kaolinite compositions. Authigenic tourmaline and relics of authigenic siderite are present. The mixture of muscovite 2M₁, paragonite, and muscovite 1M occur in the <1- μm fraction. Such a peculiar combination of dispersed rock-

Table 2. Rb–Sr age of various Riphean stratigraphic units in the southern Urals

Group, formation, subformation	Age, Ma	(⁸⁷ Sr/ ⁸⁶ Sr) ₀	MSWD	Number of data points
Yusha*	908 ± 73	0.747 ± 0.007	13.4	4
Zigaza–Komarovo*	541 ± 22	0.792 ± 0.006	0.7	4
Kataskin*	520 ± 13	0.760 ± 0.004	7.5	8
Malyi Inzer*	563 ± 22	0.728 ± 0.003	13.4	6
Kutkur and Revet*	543 ± 24	0.775 ± 0.007	8.2	8
Kuzha*	834 ± 71	0.751 ± 0.013	17.3	4
Yurmatinian**	525 ± 30	0.777 ± 0.027		27

* The values were calculated with χ^2 technique (Sokolov and Bujakaite, 1986); errors were calculated after (York, 1966).

** The values were calculated using the III model proposed by McIntyre *et al.* (1966). Samples from the Zigaza–Komarovo Formation and Kataskin, Malyi Inzer, Kutkur, and Revet subformations were involved in the calculations.

forming minerals and relationships between coarser clastic and authigenic minerals indicate repeated changes in the alteration environment. It seems likely that the subsidence epigenesis was followed by a retrograde epigenesis, weathering, redeposition of material, and a new stage of subsidence. The burial of the Yusha Formation under younger sediments promoted the conservation of mineral assemblages and their older Rb–Sr signature. Thus, an abrasion nature of the roof of the Yusha Formation can be suggested.

Rb–Sr CHARACTERISTICS OF MIDDLE RIPHEAN ROCKS IN THE SOUTHERN URALS

Lithostratigraphic Characteristics and Sampling System

The schematic Middle Riphean section in the Bashkir Meganticlinorium is shown in Fig. 1. The Yurmatinian Group overlies the Burzyanian Group with an erosion and angular unconformity. Its thickness is similar to that of the Burzyanian and is close to 5 km. The mineralogy and chemistry of secondary alterations of Riphean rocks were studied in detail by Anfimov (1977), Kagarmanova (1998), Kats (1978), and Maslov *et al.* (1999). As was demonstrated, the grade of secondary alterations is not directly correlated with the stratigraphic position. The zoning of postdiagenetic alterations of Riphean rocks of the Bashkir Meganticlinorium is controlled by the general Uralian direction. The grade of alterations decreases westward across the strike of structure and is virtually independent of stratigraphic boundaries. Similar patterns are well known. Many researchers, who studied metamorphism, metagenesis, and epigenesis, have shown that rock transformation levels cut rather than follow the stratigraphic layers. This is especially evident in tectonically active zones (Barrow, 1893; Harker, 1932; Miyashiro, 1973; Yapaskurt, 1992). It should be noted that, even within separate tectonic blocks of the southern Urals, Riphean rock alterations are distinct and depend on the

setting in the folded framework, distance from cross-cutting dikes and faults, etc.

The available samples do not allow us to give an exhaustive account of the Yurmatinian section. Nevertheless, we can confidently assume a different grade of postsedimentation alterations of Yurmatinian rocks, relative to Burzyanian rocks. Alterations more advanced than the stage of deep epigenesis are absent in Yurmatinian samples. The sedimentary texture and microstructure are retained in all clastic rocks. Only carbonate rocks experienced the recrystallization with a loss of sedimentation structures, which is a common feature at the stage of deep epigenesis.

Based on the microscopic study of thin sections of siltstones and argillites from the Zigaza–Komarovo Formation, interlayers of fine-sand dimension sediments contain quartz (62%), feldspars (23%), and lithic clasts (15%). The latter are completely recrystallized and replaced by a homogeneous aggregate of clearly delineated intergrowths of chlorite, quartz, and muscovite. It cannot be ruled out that such clasts originally consisted of andesitic glass.

Quartz and pyrite veinlets are common in the rocks. The rocks are occasionally crushed and brecciated, resulting in the loss of sedimentary textures and structures. The alteration is chiefly related to tectonic crushing and hydrothermal reworking of rocks.

Limestones, dolomites, and thin-bedded chlorite-sericite schists from the Avzyan Formation were studied. In siltstone and sandstone interlayers, the coarsening of grains is accompanied by the enrichment in feldspars up to 16%. In general, rocks of the Avzyan Formation are sharply depleted in labile components at the expense of excess quartz.

Conformable regeneration structures with the authigenic quartz are noted in thin sandy-silty layers. Sericite-rich schists are characterized by an oriented or massive structure with a chaotic distribution of sericite flakes but without a noticeable admixture of clastic

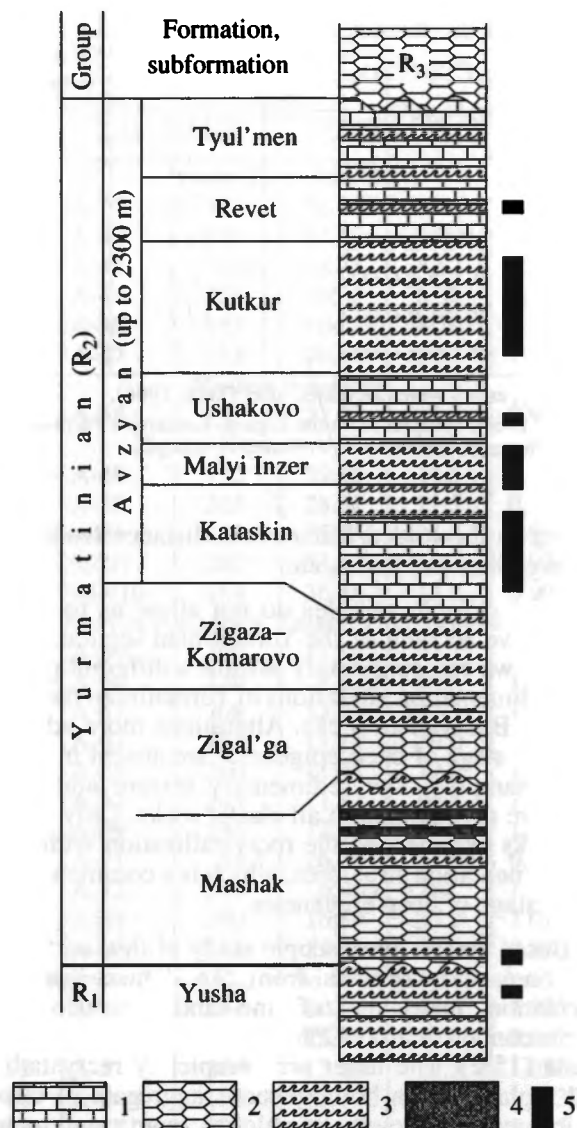


Fig. 1. Schematic column of Yurmatinian in the southern Urals. (1) Carbonate rocks; (2) sandstone; (3) argillite; (4) basalt; (5) sampling interval.

muscovite lawellas. Layers of cubic and completely oxidized pyrite clusters are abundant.

The cataclasis of limesones is demonstrated by the recrystallization of grains as a result of the pressure-induced flow and the formation of secondary structures emphasized by ribbons of elongated calcite crystals often with a polysynthetic twinning. Curvilinear twins are lacking because the stress was completely relaxed after the folding. Stylolite sutures are common.

Dolomites are also recrystallized under pressure. They often contain pockets, veins and elongated clots of coarse-crystalline anhedral quartz with a wavy extinction. Like the sandstone-hosted silicate material, dolomite is also often corroded by a late calcite.

Although the above petrographic data do not furnish an exhaustive characteristics of the Yurmatinian section, they indicate a principally distinct (relatively low-grade) postsedimentation alteration of Yurmatinian rocks, relative to the alternation of Burzyanian rocks. This conclusion is inconsistent with most data previously reported in the literature.

Intervals of argillite sampling are shown in Fig. 1. The studied Middle Riphean rocks are localized in all of the three tectonic slabs mentioned above. The most attention was paid to the stratotype section of the Avzyan Formation within the Zyuratkul slab, which is located in the easternmost and most metamorphosed part of the meganticlinorium. Samples were taken from natural outcrops along the left bank of the Bol'shoi Avzyan River in the Verkhniy Avzyan Settlement.

Rocks of the Kuzha Group were sampled using the borehole cores from the Kuzha polymetallic deposit in the westernmost part of the Zil'merdak tectonic slab.

In the Yamantau tectonic slab, we sampled the bottom of the Middle Riphean Mashak Formation and the top of the Lower Riphean Yusha Formation on the western slope of the Shatak Range (latitudinal transect along the Shatak Creek).

Results of Rb-Sr Measurements

All results are summarized in Table 1. Data points of samples from various stratigraphic units are plotted in isochron coordinates (Fig. 2). Calculated ages are also given in this figure and in Table 2. Data on the Yusha Formation and Kuzha Group are also included in the tables and plots.

Almost in all cases, the data points fit the errochron relationships. The virtually similar age of 520–560 Ma was obtained for all subdivisions of Middle Riphean, except the problematic Kuzha Group with an age of 835 ± 70 Ma. Taking into account great errors in the calculated age values, their scattering cannot be regarded as significant. The obvious difference in the initial Sr isotope ratio in various formations of the Yurmatinian Group suggests that the ratio was not completely equalized along the section at the initial moment, giving rise to the marked scattering of data points on the isochron diagram (so-called natural noise). The special statistical processing of data has been elaborated for such cases (McIntyre *et al.*, 1966). Such processing applied to the selection of 27 data points yields the age of 525 ± 30 Ma and the $(^{87}\text{Sr}/^{86}\text{Sr})_0$ ratio of 0.777 ± 0.027 .

As is shown in inset (Fig. 3), the data points are also grouped in a linear trend in the $^{87}\text{Sr}/^{86}\text{Sr}$ – $1/\text{Sr}$ coordinates. A possible interpretation of this relationship will be given below.

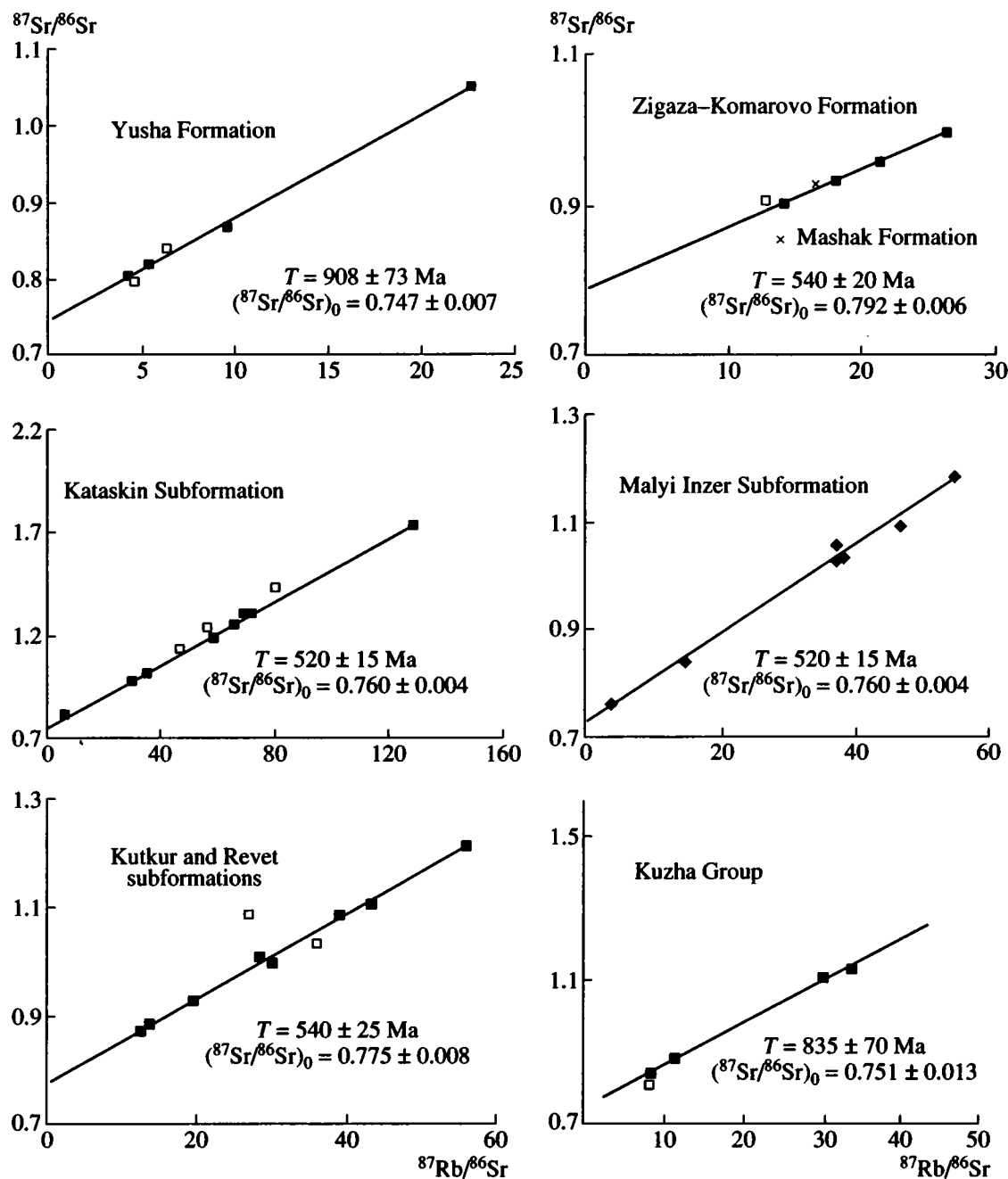


Fig. 2. Rb-Sr diagrams for whole-rock samples of argillites from various subformations of the Avzyan Formation (Yurmatinian), Yusha Formation (Burzyanian), and Kuzha Group. Open symbols denote the samples, which were omitted from calculation.

Results of K-Ar Measurements

The K-Ar measurements were carried out for a part of samples from the Avzyan Formation. The calculated age (Table 3) varies in a very wide range. Figure 4 shows that data points lie on the straight line in the calculated age - K content (in sample) coordinates. Thus, the "rejuvenation" of K-Ar age is related to the enrichment in K. As can be seen from Fig. 5, the correlation between K and Rb is lacking, and the increase in K con-

tent is not accompanied by the respective enrichment in Rb.

DISCUSSION

Rb-Sr. The most important and questionable topics in Rb-Sr geochronometry are focussed on the nature of linear trends in isochron coordinates. Such trends may be determined by the time, and the obtained relationship has an age sense. However, the same relationship

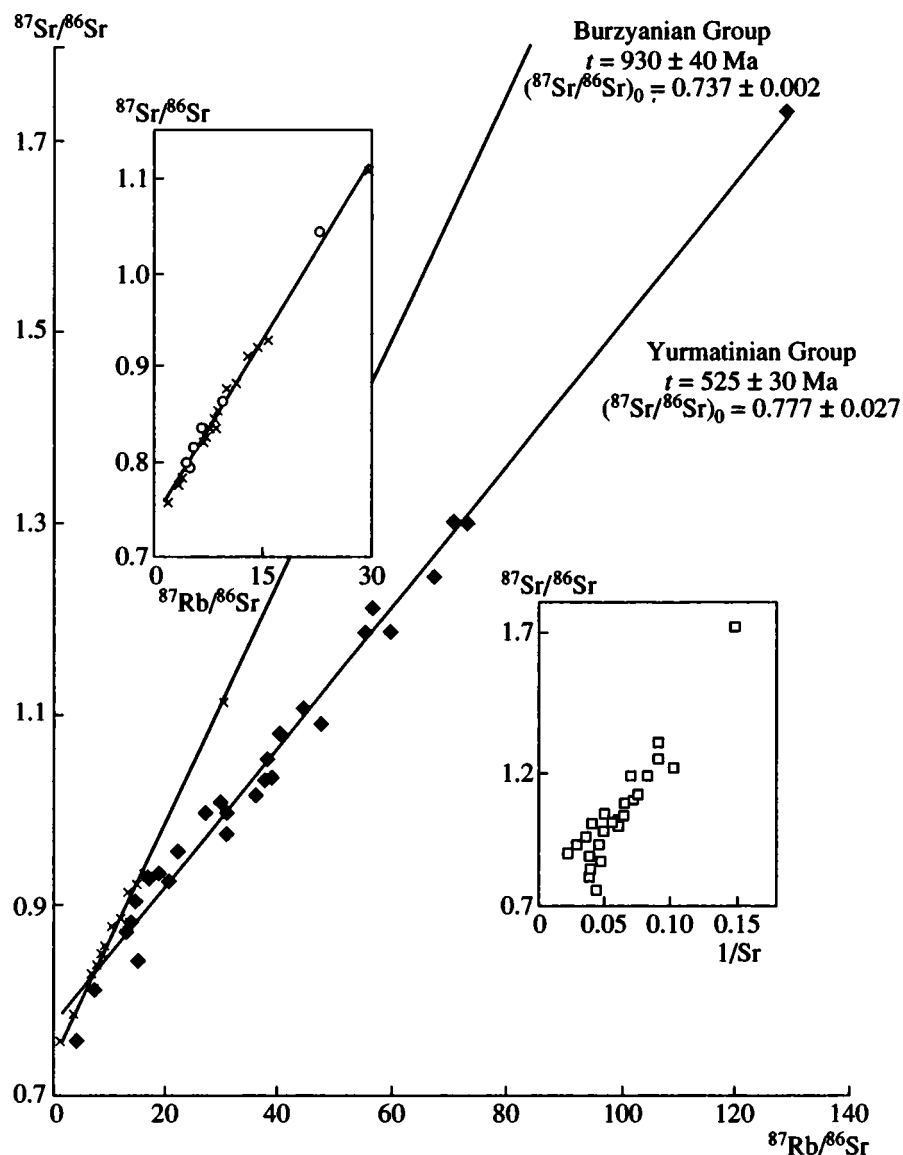


Fig. 3. Summary Rb–Sr diagrams for rocks of Middle Riphean Yurmatinian and Lower Riphean Burzyanian groups. The left inset shows the position of samples from the Yusha Formation (open circles) relative to the isochron for Burzyanian samples (crosses). The right inset demonstrates the relationship of Sr isotopic composition vs. $1/Sr$ content in samples of the Yurmatinian Group.

may be a result of two-component mixing when one component has high Rb/Sr and $^{87}Sr/^{86}Sr$ ratios (data points in the right upper region of plot) and another component is characterized by low ratios (points in the left lower region of plot). In this case, parameters of the linear trend have no geological sense. Unfortunately, with rare exceptions, there are no reliable techniques to discriminate both cases, and the problem commonly remains open. It seems that the most reliable confirmation of obtained age values resides only in the coincidence of datings based on various geochronometers and the careful study of the specific geological situation (Golovin *et al.*, 1986; Kostitsyn, 1998).

In the case of two-component mixing, data points in the coordinates $^{87}Sr/^{86}Sr$ – Sr fit the hyperbolic curve, which is transformed into a straight line with the replacement of Sr content by the $1/Sr$ value. The scattering of Rb/Sr ratio in natural samples mainly depends on the variation of Sr content rather than the Rb content, whereas points of isochron relationships plotted in the $^{87}Sr/^{86}Sr$ – $1/Sr$ coordinates are grouped along the straight line (Kostitsyn, 1998; Andreichev, 1998). In our case, the array of 27 points (Table 2, Fig. 3) is characterized by a 40% scattering of Sr contents and only 10% scattering of Rb contents. Therefore, linear relationships are observed in both coordinates.

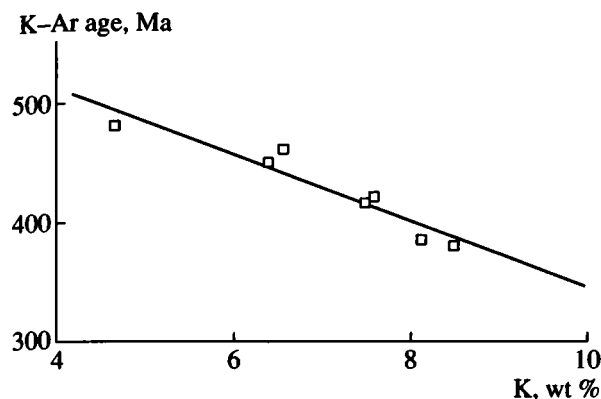


Fig. 4. Calculated K-Ar age vs. K content in samples of the Yurmatinian Group.

There is another reason to assume that we have actually obtained the Rb-Sr age of some event that affected the Yurmatinian rocks. The virtually same age of all Riphean subdivisions hardly admits any other interpretation. Finally, the similar conclusion may be drawn from the K-Ar determinations.

K-Ar. The scattering of K-Ar ages (Table 3) is commonly attributed to a partial Ar loss by minerals during their heating or other secondary effects. The Ar loss results in an apparent rejuvenation of the sample. However, the reverse linear correlation of calculated age and K content points to a quite different process. It looks likely that the rejuvenation is caused by a K gain. The epigenetic potassic metasomatism selectively proceeds within specific units during a long time, and the scattering of K-Ar age can constrain the metasomatism stage duration. Based on available scanty data, the alteration stage lasted for at least 150–200 Ma. The lower age limit of alteration stage is constrained by a possible initial K content in hydromica-bearing clayey rocks, which is conventionally estimated at 4 ± 1 wt %. The approximating straight line in Fig. 4 indicates that the K content of 4 ± 1 wt % corresponds to the age of 520 ± 30 Ma. The maximum possible K content in a sericite-only sample is about 10 wt %. Such content fits the age of ~340 Ma. It should be noted that the really measured maximal K-Ar age (480 Ma) and particularly the extrapolated to the K content of 4 wt % age value (520 Ma) are close to the average Rb-Sr age of Yurmatinian (525 ± 30 Ma). The obtained data confirm that the calculation of average K-Ar ages for rocks, which experienced long-term subsequent alterations, is hardly valid. Actual events are more likely reflected by lower and upper age limits, while the average values may be devoid of any sense.

Possible Mechanisms of the Rearrangement of Isotope Systems

The potassic metasomatism with an enrichment of clayey rocks in K is likely related to the recrystalliza-

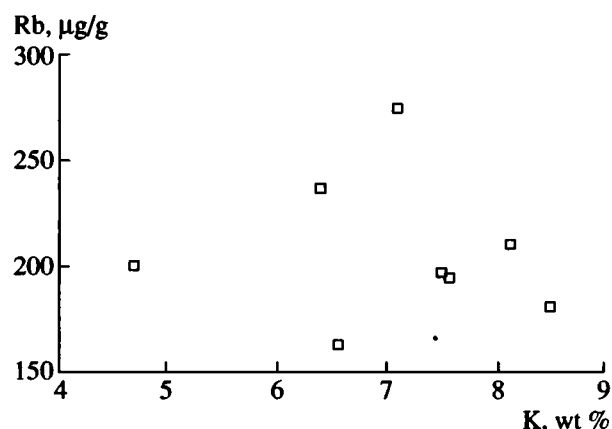


Fig. 5. Rb vs. K in samples of the Yurmatinian Group.

tion of mineral-carriers of K, and this process can result in the complete removal of previously gained radiogenic Ar, i.e., in resetting K-Ar clock to the zero level. Judging by the obtained data, this process started about 500 Ma ago and went on during at least 150–200 Ma, resulting in an enrichment in newly formed muscovite and orthoclase.

The sedimentary rock sequences, first of all, clastic rocks of arkose sandstone type and even evaporites should be regarded as a possible source of K. Therefore, we should carefully search for the traces of such sedimentary formations.

The K gain in clayey rocks during the epigenetic maturing is known rather well. This was again recently demonstrated for the case of Miocene and Oligocene sediments on the coast of Gulf of Mexico (Land *et al.*, 1997). Our data indicate that such process continues up to the metamorphic stage.

The Rb-Sr system turned out to be more stable and was conserved 525 ± 30 Ma ago. We cannot offer a reasonable interpretation of this fact. The lack of correlation between K and Rb (Fig. 5) and a small dispersion of Rb content may point to the relatively constant concentration of this element in hydrothermal solutions

Table 3. Results of K-Ar measurements for argillites of the Middle Riphean Avzyan Formation in the southern Urals

Sample no.		Subformation	K, wt %	^{40}Ar , mm ³ /g	Age, Ma
field	lab				
4513	A-23	Revet	8.49	0.138	380
4507	A-32	Kutkur	6.56	0.131	460
4492	A-34	Kutkur	7.60	0.140	420
4500	A-4	Malyi Inzer	7.50	0.136	415
4477	A-59	Kataskin	8.12	0.135	385
4483	A-69	Kataskin	6.40	0.127	450
4492	A-84	Kataskin	4.68	0.099	480

involved in rock alterations. In this case, the transformed mineral components retained the Rb content approximately at the same level. Strontium was likely inherited from the primary mineral.

As we noticed previously, the intensity of chemical alteration of rocks is correlated with the intensity of their tectonic transformation (Vinogradov *et al.*, 2000). In particular, Lower Riphean (Burzyanian) rocks of the southern Urals were altered 930 Ma ago with an averaging of the initial Sr isotope ratio within the major part of the 5-km-thick section.

The averaging of the initial Sr isotope ratio in Yurmatinian rocks was confined to separate stratigraphic, more precisely lithological units, which are distinguished from each other by the $(^{87}\text{Sr}/^{86}\text{Sr})_0$ value. This is likely caused by a somewhat less intensive epigenetic alterations of Yurmatinian rocks, relative to Burzyanian ones.

Geological implications. The substantial temporal gap between alterations of Lower and Middle Riphean sedimentary rocks in the southern Urals is the most important implication. Based on K–Ar and Rb–Sr data, the onset of epigenetic alterations in the Yurmatinian Group is registered about 525 Ma B.P. It should be reminded that the underlying Burzyanian Group was altered at 930 Ma B.P. This implies that both series were juxtaposed in the section by tectonic processes. However, it is hardly reasonable to assume that the tectonic juxtaposition resulted in a simple doubling of section, because Lower and Middle Riphean rocks are distinct in chemistry. As can be seen from Fig. 2, the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio ranges from 0 to 30 in Yusha, Zigaza-Komarove, and Kuzha argillites but reaches 30–130 in Avzyan (Katanskin) rocks. Hence, rocks of both groups had distinct initial compositions, or they underwent distinct epigenetic alterations. Therefore, Burzyanian and Yurmatinian sequences hardly cannot be assumed as a common or a doubled section.

The concept of different grades of regional metamorphism across the meganticlinorium can furnish an alternative explanation for the temporal gap in alterations of Lower and Middle Riphean rocks.

Among the studied stratigraphic units, only the Kuzha Group can be referred to the western-type section with the maximal alteration at the stage of deep epigenesis. Lower Riphean rocks of the Yusha Formation, as well as Middle Riphean Zigaza-Komarovo and Avzyan formations (stratotype section in the Verkhniy Avzyan Settlement area) in the central Bashkir Meganticlinorium were altered to a greater extent that can be defined as a stage transitional between deep high-pressure epigenesis and initial metagenesis.

Assuming the commonly accepted Yurmatinian age of the Kuzha Group, it should be concluded that the first stage of deep alterations, which most likely affected the entire Middle Riphean sedimentary basin, terminated 835 ± 70 Ma ago. Subsequently, Yurmatinian rocks, except the Kuzha Group rocks, subsided

again and underwent a severe lateral compression. The peak of this process is registered by the general Rb–Sr errorchron of 525 ± 30 Ma. Judging by K–Ar datings, the process was terminated about 340 Ma ago probably due to the exhumation of metamorphic rocks of the Central Uralian Uplift during the Paleozoic collision.

It is evident that the further study of Yurmatinian sequences over a wider territory is needed to make a more convincing conclusion.

A sharp temporal gap is also outlined between the Yurmatinian and Karatavian sequences. The Pb–Pb age of carbonates and Rb–Sr age of clay fractions from the Inzer Formation of Karatavian yielded 800–850 Ma (Gorokhov *et al.*, 1995; Ovchinnikova *et al.*, 1995, 1998). Our tentative study of whole-rock samples of Upper Riphean argillites in the southern Urals gave the same results. Principal differences in K–Ar ages of Yurmatinian and Karatavian sedimentary rocks were also noted by Kagarmanova (1998).

CONCLUSION

Middle Riphean rocks of the Yurmatinian Group in the Bashkir Meganticlinorium underwent secondary epigenetic alterations, which, in particular, were accompanied by a potassic metasomatism with the local gain of up to 8.5 wt % K. The potassic metasomatism, which started about 520 Ma ago, affected specific lithological units and lasted for at least 150 Ma.

Substantial temporal gaps are registered between stages of the alteration of various groups of Riphean sedimentary rocks. It may be inferred that each of three Riphean groups was affected by its own alteration stage. It cannot be ruled out that these groups do not form a common stratigraphic succession.

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Origin of the Belomorian Chupa Gneiss in the Light of New Lithogeochemical Data

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Abstract—The stratotype Chupa Sequence, which makes up the synonymous tectonic nappe and is a member of oldest (Late Archean) rocks in the Belomorian Mobile Belt, is scrutinized. The nappe is mainly composed of the migmatized, coarse-grained garnet–biotite gneiss with kyanite. Relic formations are represented by lenses of the fine-grained (possibly primary) garnet–biotite gneiss. Fine-grained gneisses generally represent primary sedimentary formations, while metadacites are rare. The kyanite-bearing gneiss is presumably a restitic rock produced by migmatization. Chupa metasediments are represented by immature (low-differentiated) metagraywackes and are akin to metaterigenous rocks from Late Archean greenstone belts of Karelia (Kostomuksha) and Canada (Quebec). The provenance of metasediments comprises the following three components: tonalite (dacite) 70%, mafic rocks 20%, and ultramafic rocks 10%. The Chupa metagraywacke presumably deposited in a fore-arc basin.

The Chupa aluminous gneiss has long attracted the attention of researchers, since it governs the spatial distribution of mica-bearing pegmatites. Therefore, the gneiss zone, which extends over 250 km from Lake Engozero in south to deposits of the Rikolatva district in north, is better surveyed than other sectors of the Belomorian Mobile Belt (Fig. 1). Aluminous gneisses of the region, which were identified as the Chupa Formation during survey in the 1950s, were referred to as the Chupa nappe within the Late Archean Belomorian allochthon at the terminal 1980s (Miller and Mil'kevich, 1995).

The Chupa nappe generally includes the coarse-grained (schistosed and migmatized) garnet–biotite gneiss often containing kyanite. Relic bodies are represented by thin lenses and strata of the unaltered (i.e., nonmigmatized), fine-grained garnet–biotite gneiss. The amphibole-bearing gneiss and amphibolite are subordinate. Gneisses include concordant veinlets and veins of biotitic tonalite with xenoliths of the Chupa gneiss. Tonalites account for 30 to 80% of the nappe section.

Isotope geochronological data suggest that the Chupa gneiss can be considered a member of oldest (Late Archean) rocks in the White Sea (Belomorian) region. The U–Pb zircon datings for garnet–biotite gneisses from the Tupaya Guba district are estimated at 2855 Ma and interpreted as the age of granulite metamorphism (Bibikova *et al.*, 1993; Lobach-Zhuchenko *et al.*, 1993). The available Sm–Nd model age of the garnet–biotite gneiss protolith (Bibikova *et al.*, 1996; Timmerman and Daly, 1995) indicates that rocks of the provenance formed between 2.86 and 3.01 Ma B.P.

The Chupa gneiss bears distinct traces of three metamorphic stages recognized within the Belomorian Mobile Belt (Bibikova *et al.*, 1997; Drugova, 1996; Glebovitskii *et al.*, 1996; Lobach-Zhuchenko *et al.*, 1993; Volodichev, 1975, 1990). The early Rebolian, moderate-pressure granulite metamorphism is considered the oldest stage (2850 Ma). The late Rebolian, high-pressure amphibolite (locally granulite) metamorphism is assigned to the Late Archean collision (2660–2730 Ma). The Svecofennian collision (1800–1900 Ma) was responsible for the zonal, high-pressure amphibolite metamorphism followed by the formation of pegmatites in the Chupa nappe zone. In contrast to the common concept, Ruch'ev (1992) believes that the early Rebolian metamorphism reflected in fine-grained garnet–biotite gneisses was characterized by lower pressures emphasizing prograde evolution toward the late Rebolian stage.

The composition and primary nature of aluminous gneisses in the Chupa nappe are crucial for the geodynamic modeling. Although publications concerning this aspect are numerous, the origin of the Chupa gneiss still remains a debatable problem. E.P. Chuikina and her proponents (Gorlov, 1967; Shurkin *et al.*, 1962) assume that the Chupa gneiss is a product of strongly metamorphosed sediments, primarily pelites (Bibikova *et al.*, 1997). Other researchers (Golovanova, 1983; Volodichev, 1969; 1990; Zarubin, 1969) suggest that the gneisses were produced by ultrametamorphic and metasomatic transformations of the fine-grained gneiss. According to Volodichev (1990), the latter represents a metavolcanic rock of the intermediate (to a lesser extent acid or basic) composition.

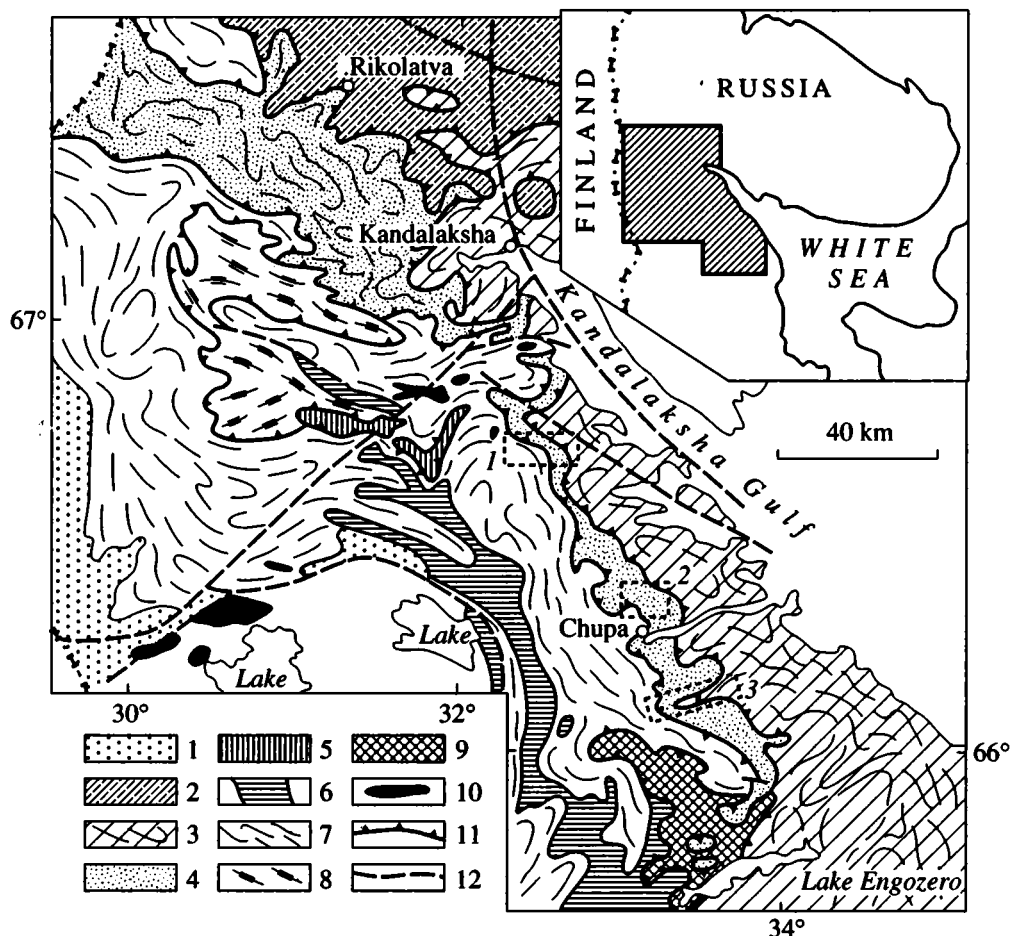


Fig. 1. Tectonic scheme of the central Belomorian Mobile Belt. (1) Early Proterozoic troughs; (2) Svecofennian (Lapland) allochthon, Rikolatva nappe; Late Archean (Belomorian) allochthon; (3) Khetolamba nappe (tonalite with mafic and ultramafic bands), (4) Chupa nappe (aluminous gneiss with tonalite injections), (5) Kalikorvi nappe (amphibolite with aluminous gneiss horizons), Kovdozero nappe (allochthonous margin of the Karelian Craton) including the (6) Keret greenstone belt (metabasalt and intermediate tuff) and (7) tonalite-rich infracrustal complex, (8) Orijarvi nappe (tonalite), (9) Maiozero nappe (amphibolite with aluminous gneiss horizon); (10) Early Proterozoic gabbro-norite-lherzolites; (11) regional displacement planes restricting the nappes; (12) faults. The box outlines studied sectors within the Chupa nappe: (1) Tupaya Guba, (2) Pulong, (3) Keleinaya Guba.

The problem resides in the following: gneisses of the study region are almost devoid of primary structures and practically undecipherable by conventional geological methods. Therefore, the Chupa gneiss origin is diversely interpreted. However, in works devoted to this region, except (Ruch'ev, 1997), this aspect was not systematically investigated, and the geochemistry was not sufficiently studied.

The present work is an attempt to solve this problem by geochemical methods. The Chupa gneiss was studied in sections exposed in the following three sectors (Fig. 1, 1–3): (1) Tupaya Guba sector (between Tupaya Guba of Lake Kovdozero and Lake Seryak); (2) Pulong sector (to the east of the Chupa Settlement); and (3) Keleinaya Guba sector (Lake Loukh area). The Pulong section, which was most appropriate for reconstructing the primary composition of rocks, is well exposed in a stratotype locality and incorporates several outcrops of

relic fine-grained gneissic bodies. The section is also characterized by a minimal impact of the Svecofennian deformation and metamorphism. Therefore, the number of metamorphic stages, which could alter the primary composition of rocks, is reduced. The coarse-grained, migmatized garnet-biotite gneiss with kyanite is abundant here. It was possibly developed during the Late Rebolian, high-pressure amphibolite metamorphism. The fine-grained gneiss is observed as local relic bodies of an earlier, insufficiently studied metamorphic stage.

GENERAL CHARACTERISTICS OF THE PULONG SECTOR

The geological setting of the Pulong sector is governed by two intricate Svecofennian domes (Karelian dome in the northwest and Chupa dome in the south-

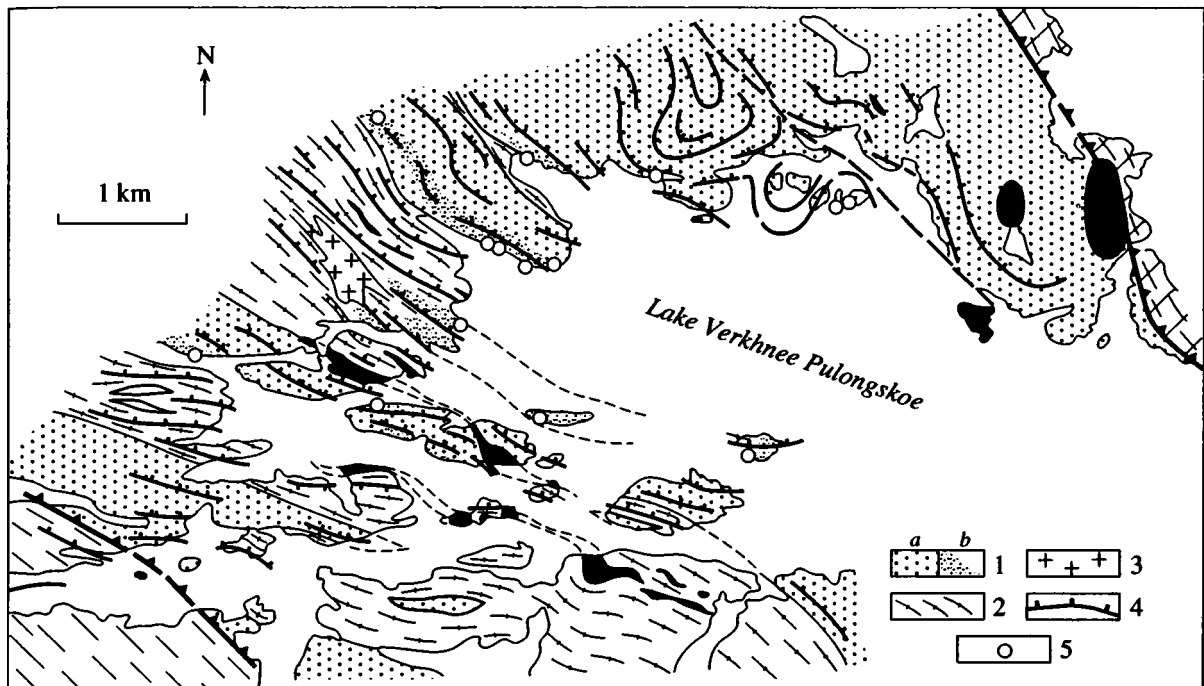


Fig. 2. Schematic geological map of the Pulong sector. (1) Coarse-grained kyanite-garnet-biotite gneiss (a) migmatized to a variable extent or (b) with abundant relics of the fine-grained garnet-biotite gneiss; (2) tonalite; (3) late granite; (4) generalized strike and dip directions of schistosity and lamination (metamorphic and migmatitic); (5) sampling location. Other legends as in Fig. 1.

east). Hinges of these domes host large muscovite pegmatites. The sector is apparently characterized by a simple structure. The Chupa gneiss primarily dips toward the northeast under the Khetolamba nappe and, in turn, is underlain by tonalites of the Kovdozero nappe (Fig. 2). Small folds on the northern coast of Lake Verkhnee Pulongskoe do not appreciably distort the general monoclinial setting of the Chupa nappe, which is approximately 2 km thick in this section. The entire monoclinial area extending from Kovdozero to Engozero is composed of nappes.

The Chupa nappe mainly consists of medium- and coarse-grained, kyanite-bearing, garnet-biotite gneisses intruded by tonalite veins. Thin boudins are composed of the subordinate biotite-garnet-hornfels gneiss and garnet amphibolite. The kyanite-garnet-biotite gneiss includes a small amount of the unaltered (fine-grained and granoblastic) garnet-biotite gneiss. Relics of the latter rock are generally preserved in the central part of the Chupa nappe but disappear at the bottom and top of the nappe presumably owing to an intensification of rock alteration. Lenticular and stratiform bodies of the fine-grained gneiss, 10 cm to n m thick, sometimes extend along the strike over tens of meters. In the presented map (Fig. 2), adjacent relic bodies are united; therefore, the dimension is slightly exaggerated. On the whole, relic bodies account for up to 1% of the total nappe thickness. These rocks are usually non-layered, but a fine-banded structure is observed at some exposures. The bands, 5 to 10 cm thick, are asymmetric

and resemble the sedimentary rhythm. The leucocratic gneiss grades into the biotite-rich melanocratic variety that has a sharp contact with the next leucocratic gneiss band.

Numerous well-washed exposures on the lake coast demonstrate that the coarse-grained gneiss is developed after the fine-grained variety. This alteration is primarily manifested by the recrystallization of minerals, coarsening of rocks, and development of migmatitic veins that are gradually thickened and increased in number. The melanosome is simultaneously characterized by an enrichment in biotite, development of kyanite, depletion in quartz and plagioclase, and stronger schistosity. Thus, we can actually observe the process of restite formation (Fig. 3). These relationships, coupled with geochemical data presented below, suggest that only the fine-grained garnet-biotite gneiss can be considered the primary rock.

CHEMICAL CHARACTERISTICS

Among the above-listed gneiss varieties in the Chupa nappe, we examined forty samples for the major and trace element contents and seven samples for REE concentrations. Sampling sites are shown in Fig. 2. Major elements were determined by the X-ray spectral analysis, according to the procedure developed at the VSEGEI (Karpinskii All-Russia Research Institute of Geology, St. Petersburg). The measurement of trace elements by a VRA-30 X-ray microprobe and the quan-

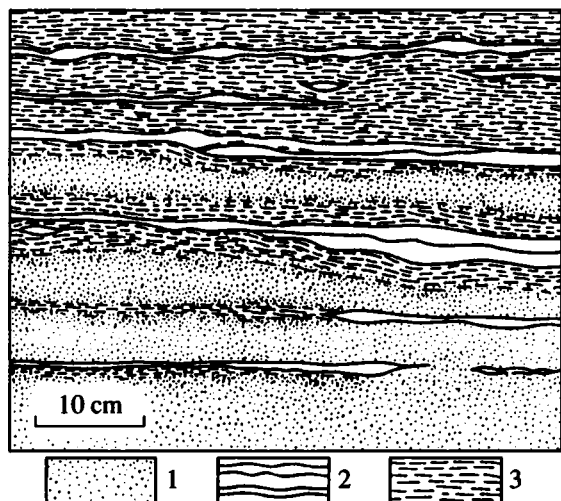


Fig. 3. Typical relationship between the fine-grained garnet-biotite gneiss and the coarse-grained garnet-biotite gneiss with kyanite (drawing based on photomicrograph). (1) Fine-grained garnet-biotite gneiss; (2) migmatitic veinlets; (3) coarse-grained garnet-biotite with kyanite.

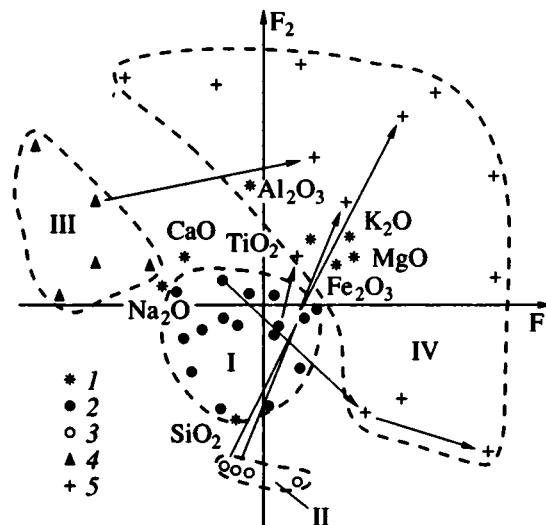


Fig. 4. The F_1 - F_2 plot for rocks from the Chupa Sequence. (1) Factor loads; factor designations: (2) metasiltsone, (3) metasandstone (rock names are given according to Neelov's classification, see Fig. 7), (4) metadacite, (5) migmatized, coarse-grained garnet-biotite gneiss with kyanite. (I-III) domains of the fine-grained garnet-biotite gneiss; (IV) domain of the coarse-grained kyanite-garnet-biotite gneiss. Lines connect datapoints of contacting rock varieties.

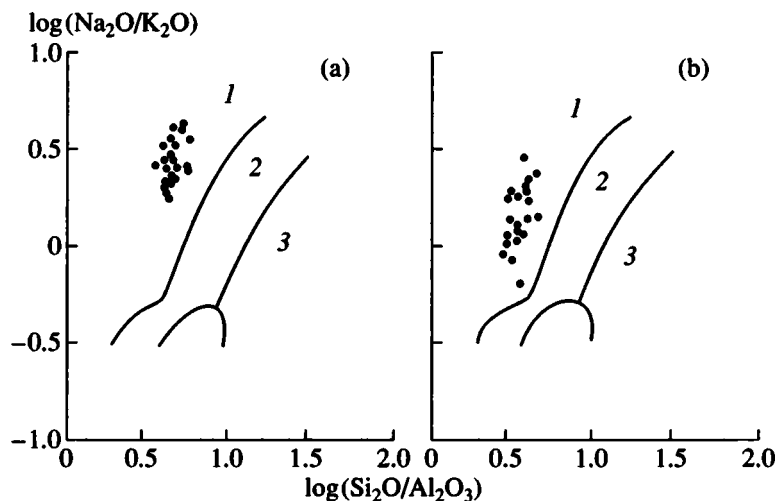


Fig. 5. The $\log(\text{Na}_2\text{O}/\text{K}_2\text{O})$ - $\log(\text{SiO}_2/\text{Al}_2\text{O}_3)$ classification plot (Pettijohn *et al.*, 1973) for metaterigenous rocks from (a) Chupa and (b) Kostomuksha. Compositional domains: (1) graywacke, (2) lithic wacke, (3) arkose.

titative analysis of rare earth elements by the INAA method were performed in the laboratory of IGGD (Institute of Precambrian Geology and Geochronology, St. Petersburg).

Compositions of all selected rock samples are presented in the table and plotted on the F_1 - F_2 diagram (based on the method of major components), Pettijohn's and Neelov's classification diagrams, and Harker's variation diagrams.

On the F_1 - F_2 diagram (Fig. 4) based on major elements, the fine-grained gneiss is subdivided into three

genetic groups (I-III). The migmatized, coarse-grained garnet-biotite gneiss with kyanite can be identified as a separate group IV.

The group III is geochemically akin to dacites (table). Groups I and II are compositionally similar (except for slight SiO_2 and Al_2O_3 variations). They differ from dacites by higher values of $\text{Fe}_2\text{O}_{3\text{tot}}$, MgO/CaO , Cr (as much as 300 ppm), and other iron group elements. This kind of geochemical signature is unusual for igneous gneisses. Therefore, we referred these gneisses to as

Comparison of average compositions of rocks from the Chupa Sequence with metasediments from Late Archean greenstone belts

Component	Chupa				Kostomuksha	Quetico	Archean graywacke
	metasiltstone	metasandstone	metadacite	Ky-Gr-Bt gneiss			
SiO ₂	68.00	71.22	66.35	62.84	63.93	64.72	67.79
TiO ₂	0.71	0.66	0.52	0.93	0.56	0.56	0.56
Al ₂ O ₃	14.67	12.62	17.12	17.91	15.39	15.36	15.44
Fe ₂ O ₃	5.6	5.5	3.69	7.06	7.19	6.60	6.53
MnO	0.05	0.05	0.02	0.07	0.03	0.09	0.07
MgO	2.33	2.16	1.15	3.90	2.62	2.76	2.54
CaO	3.08	3.04	4.48	2.51	2.07	2.77	1.90
Na ₂ O	3.79	3.33	4.81	2.93	4.04	3.50	4.26
K ₂ O	1.53	1.04	1.00	2.41	2.28	2.36	1.40
P ₂ O ₅	0.09	0.13	0.24	0.13	0.01	0.17	0.09
L.O.I.	0.50	0.40	0.50	0.50	1.88		
Ba	340	294	354	475	630	639	418
Rb	62	42	27	86	97	83	50
Sr	210	232	474	211	309	340	357
Zr	121	122	119	124	130	142	130
Y	16	16	14	20	15	14	17
Nb	8	7	8	9	8		7
Cr	288	286	83	364	143	175	145
V	115	101	54	179	103		116
Ni	96	72	37	137	52		59
Co	27	22	12	37	23		
n	17	4	3	16			
CIA	53	51		59	56	58	60
Cr/Ti	0.074	0.092		0.080	0.043	0.048	0.043
Zr/Y	7.65	7.59		6.50	8.8	9.72	7.65
Total REE	79.12	74.04	95.31		91.95	122.9	97.00

Note: Major elements are given in wt %, trace elements are given in ppm. Total Fe is presented in the form of Fe₂O₃. CIA = 100 × [Al₂O₃/(Al₂O₃ + CaO + Na₂O + K₂O)], mol % (Nesbitt and Young, 1982). (n) Number of analyses. Data on metagraywackes from Kostomuksha (Mil'kevich and Myskova, 1998) and Quetico (Sawyer, 1986) are average values. The Archean graywacke is represented by Sample YK-2 from the Slave Province (Jenner *et al.*, 1981).

primary sedimentary rocks. This conclusion is supported by correlation data presented below.

Based on Pettijohn's classification (Pettijohn *et al.*, 1973), both metasediment groups are assigned to graywackes (Fig. 5a).

The migmatized, coarse-grained garnet-biotite gneiss with kyanite lacks any common features with fine-grained gneisses (groups I-III). It is developed in all rock varieties, including metadacites (Fig. 4). Maximal contents of Al₂O₃, K₂O, MgO, Rb, and iron group elements in the coarse-grained variety are typical of restites that are formed during migmatization. The distribution trend of elements during migmatization is demonstrated in Fig. 6. One can easily notice the loss of SiO₂, Na₂O, and CaO but gain of Al₂O₃, MgO,

Fe₂O_{3 tot}, TiO₂, and K₂O. This pattern is also typical of the sedimentary differentiation. Therefore, we cannot always confidently determine the nature of coarse-grained gneisses. In each specific case, one should carefully examine direct geological relationships between various rock types and their structures.

A more detailed classification of the Chupa metagraywacke is based on Neelov's *ab* diagram (Neelov, 1980) and presented in Fig. 7. It reveals a weak differentiation of the Chupa metasediment from siltstones (group I) to sandstones (group II). For convenience sake, these rocks are hereafter called metasiltstones and metasandstones. Owing to a stronger alteration, datapoints of the coarse-grained gneiss are shifted on the *ab* plot toward the domain of more aluminous and

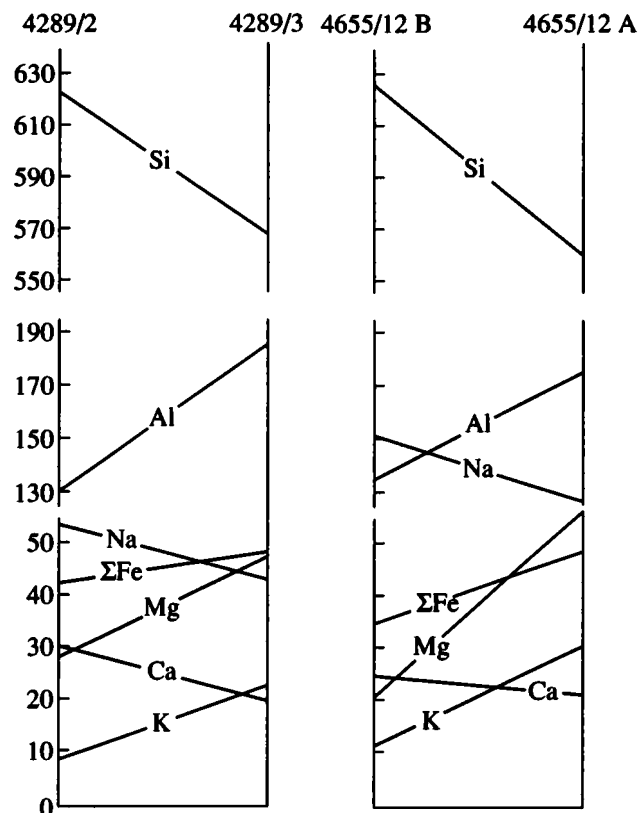


Fig. 6. Compositional variations in the fine-grained garnet-biotite gneiss (samples 4289/2 and 4655/12A) during its transformation into the coarse-grained kyanite-garnet-biotite gneiss (samples 4289/3 and 4655/12B). Chemical compositions of rocks were determined according to Bart's method.

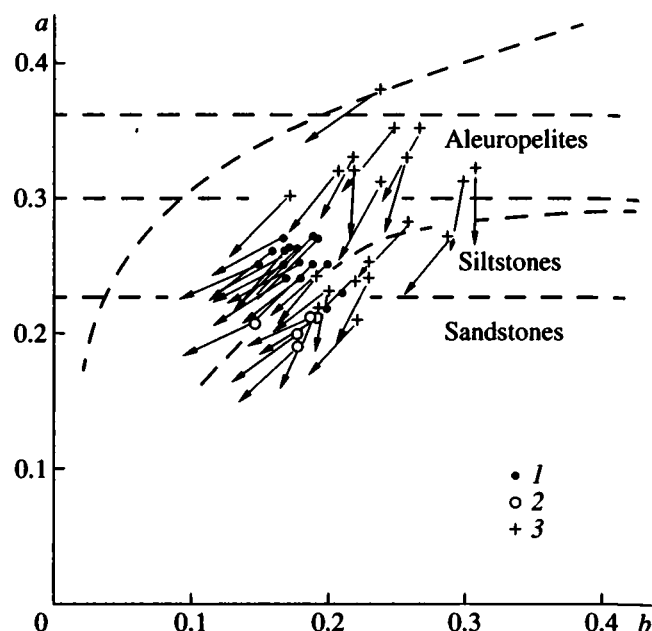


Fig. 7. The *ab* plot for rocks of the Chupa Sequence. *a* = Al/Si (alumina modulus); *b* = (Fe₂O₃ + FeO + MnO + MgO + CaO)/1000 (reflects the total content of melanocratic minerals). Vectors designate parameters characterizing the alkalinity of rocks: vector length, *n* = K + Na; vector slope, *k* = K/(K + Na). Petrochemical characteristics are expressed in atomic amounts. (1) Metasiltstone; (2) metasandstone; (3) coarse-grained kyanite-garnet-biotite gneiss. Metasediments of the Chupa Sequence are characterized by a moderate alkalinity (*n* = 0.14) and high Na₂O content, relative to K₂O (*k* = 0.14–0.28).

mafic rocks (Fig. 7). The aluminous modulus *a* varies from 0.19–0.27 in the fine-grained gneiss to 0.21–0.38 in the migmatized coarse-grained variety. It is worth noting that compositional variation trends during migmatization and sedimentary differentiation are similar. In both cases, one can observe an increase in Al₂O₃, K₂O, and mafic elements. Therefore, we can obtain an erroneous (more aluminous and mafic) image in reconstructions of the primary composition of migmatized sedimentary sequences.

Datapoints of fine-grained and coarse-grained gneisses on Harker's diagrams are characterized by diverse elemental differentiation trends (Fig. 8). In the fine-grained gneiss, SiO₂ has a negative correlation with K₂O (correlation coefficient, *R* = –0.82), MgO (–0.69), Al₂O₃ (–0.44), TiO₂ (–0.42), and Fe₂O₃_{tot} (–0.38) but a weak positive correlation with Na₂O (+0.33) and CaO (+0.14). At the same time, K₂O reveals a positive correlation with MgO (+0.70) and Al₂O₃ (+0.42). This correlation style actually matches the process of weathering product differentiation, during which sediments are fractionated into psammites (SiO₂, Na₂O, and CaO) and pelites (Al₂O₃, MgO, and K₂O). The strongest cor-

relation of K₂O, however, is observed with MgO rather than Al₂O₃, suggesting that the composition of metasediments is governed to a greater extent by the source rock composition rather than the weathering intensity. Therefore, Cr (together with other iron group elements) has a negative correlation with Al₂O₃ (–0.74) but a positive correlation with Fe₂O₃_{tot} (+0.78) and MgO (+0.30). This geochemical pattern was inherited from mafic and ultramafic rocks. Generally, Cr and Ni are preferentially concentrated in clayey rocks and are covariant to MgO having a positive correlation with Al₂O₃ (Camire *et al.*, 1993; Mil'kevich and Myskova, 1998). Owing to a high mobility during weathering, CaO and Na₂O have very weak correlations with all elements. However, sufficiently high contents of these elements in rocks testify to a low maturity of the provenance and insignificant transportation of the material (feldspars are not completely decomposed).

The weak chemical weathering is also indicated by significant positive correlations between MgO, K₂O, and Al₂O₃. The coarse-grained gneiss is distinguished from the fine-grained variety by a more intricate correlation between elements: SiO₂ has a significant nega-

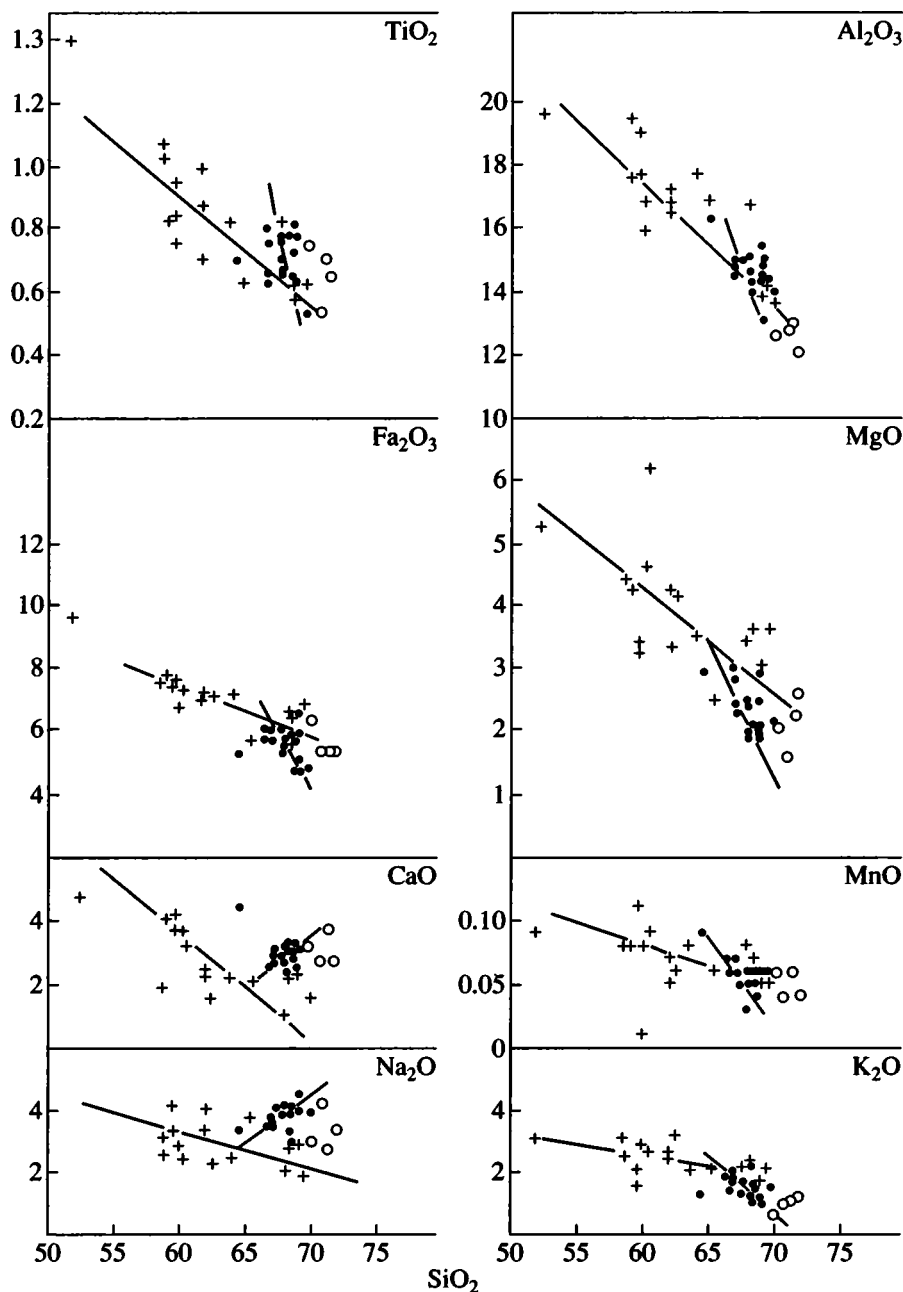


Fig. 8. Variation plots for the Chupa Sequence gneiss. Legend as in Fig. 7.

tive correlation with CaO and a weak negative correlation with Na_2O . Correlations between other elements are similar in both groups, although the significance can differ. These observations support our assumption about a secondary nature of the migmatized, coarse-grained garnet-biotite gneiss with kyanite. Hence, we cannot refer to the alumina-rich gneiss as the most mature pelite component in the Chupa Sequence. As shown above, the high alumina content in it is presumably caused by processes of restite formation during the migmatization. Therefore, only the unaltered fine-

grained gneiss can be referred to as primary rock in the study region.

DISCUSSION

Based on the geology and geochemistry of studied rocks, we can conclude that only the fine-grained gneiss of mostly sedimentary origin matches the primary composition. The scanty dacite-type species in the region are not discussed in this work. Although direct observations are extremely rare, the presence of layering in the Chupa Sequence cannot be ruled out.

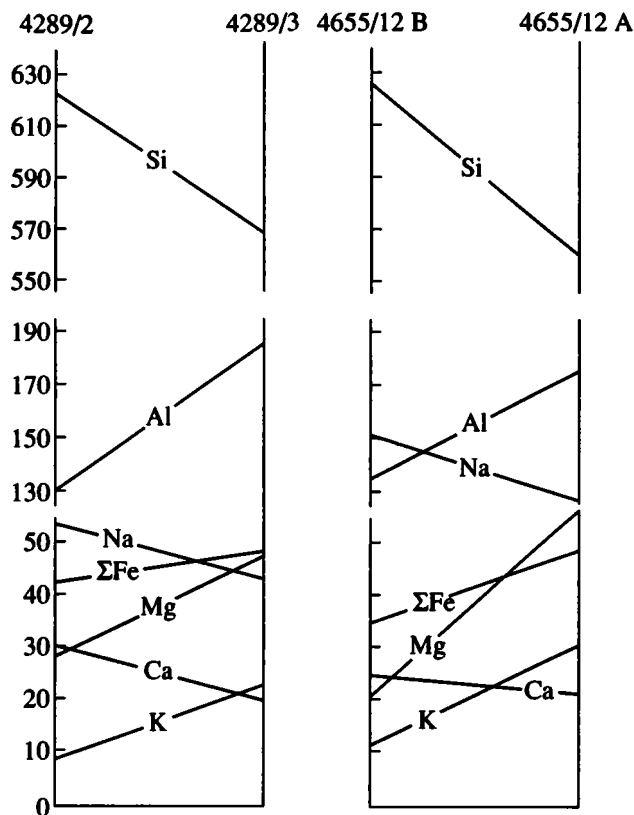


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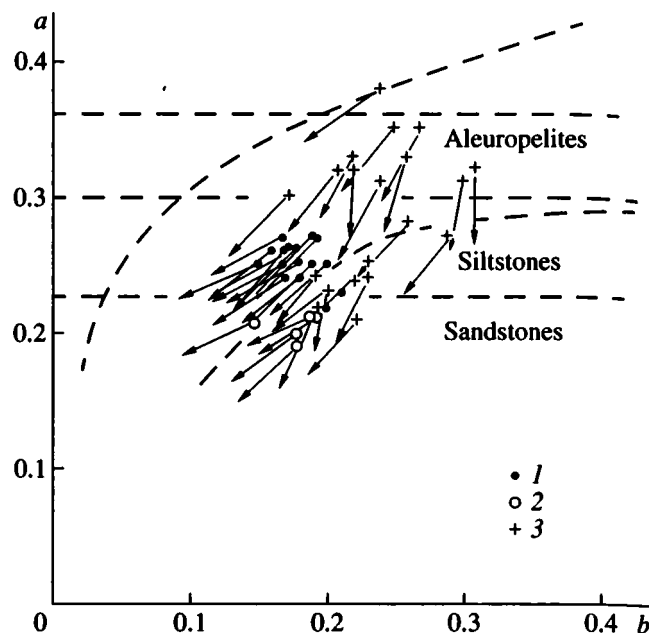


Fig. 7. The *ab* plot for rocks of the Chupa Sequence. *a* = Al/Si (alumina modulus); *b* = (Fe₂O₃ + FeO + MnO + MgO + CaO)/1000 (reflects the total content of melanocratic minerals). Vectors designate parameters characterizing the alkalinity of rocks: vector length, *n* = K + Na; vector slope, *k* = K/(K + Na). Petrochemical characteristics are expressed in atomic amounts. (1) Metasiltstone; (2) metasandstone; (3) coarse-grained kyanite-garnet-biotite gneiss. Metasediments of the Chupa Sequence are characterized by a moderate alkalinity (*n* = 0.14) and high Na₂O content, relative to K₂O (*k* = 0.14–0.28).

mafic rocks (Fig. 7). The aluminous modulus *a* varies from 0.19–0.27 in the fine-grained gneiss to 0.21–0.38 in the migmatized coarse-grained variety. It is worth noting that compositional variation trends during migmatization and sedimentary differentiation are similar. In both cases, one can observe an increase in Al₂O₃, K₂O, and mafic elements. Therefore, we can obtain an erroneous (more aluminous and mafic) image in reconstructions of the primary composition of migmatized sedimentary sequences.

Datapoints of fine-grained and coarse-grained gneisses on Harker's diagrams are characterized by diverse elemental differentiation trends (Fig. 8). In the fine-grained gneiss, SiO₂ has a negative correlation with K₂O (correlation coefficient, *R* = –0.82), MgO (–0.69), Al₂O₃ (–0.44), TiO₂ (–0.42), and Fe₂O₃_{tot} (–0.38) but a weak positive correlation with Na₂O (+0.33) and CaO (+0.14). At the same time, K₂O reveals a positive correlation with MgO (+0.70) and Al₂O₃ (+0.42). This correlation style actually matches the process of weathering product differentiation, during which sediments are fractionated into psammities (SiO₂, Na₂O, and CaO) and pelites (Al₂O₃, MgO, and K₂O). The strongest cor-

relation of K₂O, however, is observed with MgO rather than Al₂O₃, suggesting that the composition of metasediments is governed to a greater extent by the source rock composition rather than the weathering intensity. Therefore, Cr (together with other iron group elements) has a negative correlation with Al₂O₃ (–0.74) but a positive correlation with Fe₂O₃_{tot} (+0.78) and MgO (+0.30). This geochemical pattern was inherited from mafic and ultramafic rocks. Generally, Cr and Ni are preferentially concentrated in clayey rocks and are covariant to MgO having a positive correlation with Al₂O₃ (Camire *et al.*, 1993; Mil'kevich and Myskova, 1998). Owing to a high mobility during weathering, CaO and Na₂O have very weak correlations with all elements. However, sufficiently high contents of these elements in rocks testify to a low maturity of the provenance and insignificant transportation of the material (feldspars are not completely decomposed).

The weak chemical weathering is also indicated by significant positive correlations between MgO, K₂O, and Al₂O₃. The coarse-grained gneiss is distinguished from the fine-grained variety by a more intricate correlation between elements: SiO₂ has a significant nega-

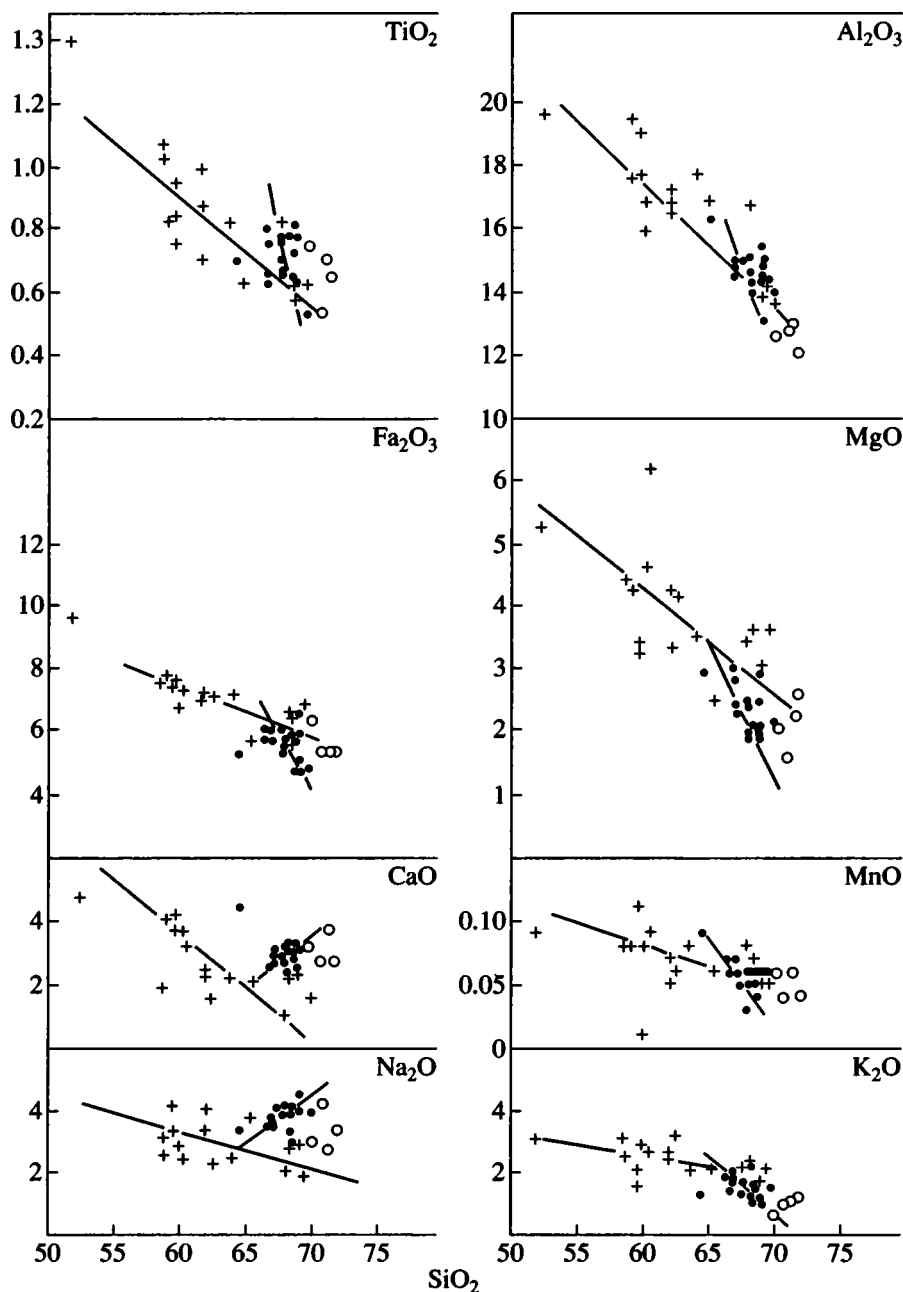


Fig. 8. Variation plots for the Chupa Sequence gneiss. Legend as in Fig. 7.

tive correlation with CaO and a weak negative correlation with Na₂O. Correlations between other elements are similar in both groups, although the significance can differ. These observations support our assumption about a secondary nature of the migmatized, coarse-grained garnet–biotite gneiss with kyanite. Hence, we cannot refer to the alumina-rich gneiss as the most mature pelite component in the Chupa Sequence. As shown above, the high alumina content in it is presumably caused by processes of restite formation during the migmatization. Therefore, only the unaltered fine-

grained gneiss can be referred to as primary rock in the study region.

DISCUSSION

Based on the geology and geochemistry of studied rocks, we can conclude that only the fine-grained gneiss of mostly sedimentary origin matches the primary composition. The scanty dacite-type species in the region are not discussed in this work. Although direct observations are extremely rare, the presence of layering in the Chupa Sequence cannot be ruled out.

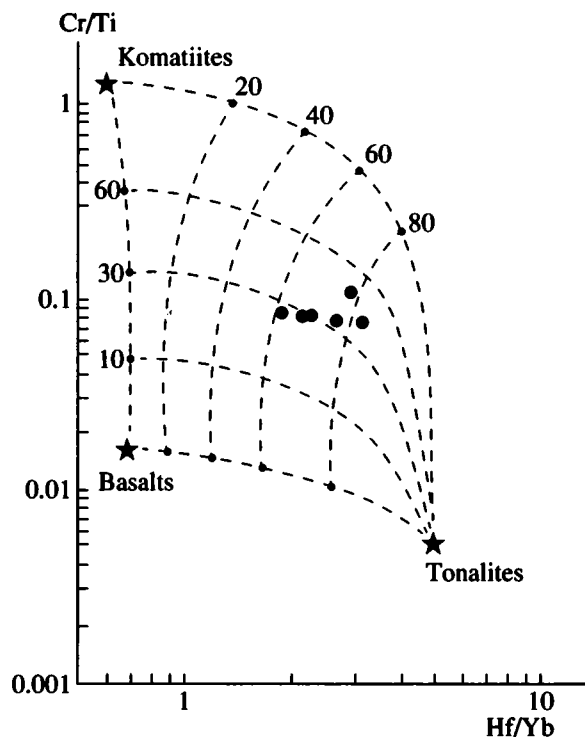


Fig. 9. Plot reflecting the composition of metaterrigenous rock provenance, based on the method described in (La Fleche and Camire, 1996). Solid dots show variations in the Chupa metagraywacke composition.

The layering is suggested by correlations between elements. The negative correlation of SiO_2 with most major compounds (K_2O , Al_2O_3 , MgO , TiO_2 , and $\text{Fe}_2\text{O}_{3\text{ tot}}$) and the positive correlation of K_2O with MgO and Al_2O_3 reflect the trend of terrigenous material fractionation into psammitic and pelitic interlayers. However, since K_2O has a stronger correlation with MgO rather than Al_2O_3 , we can suppose that the composition of interlayers was considerably governed by the source rock composition. This inference is also supported by the fact that the geochemistry of Cr is likely to be inherited from mafic and ultramafic rocks. It has a negative correlation with Al_2O_3 but a positive correlation with $\text{Fe}_2\text{O}_{3\text{ tot}}$ and MgO . Generally, Cr and Ni are concentrated in clayey interlayers and have a positive correlation with Al_2O_3 . The chemical composition of Chupa metasediments is typical of rocks with a low grade of maturity. The quantitative assessment of the chemical weathering intensity in provenance rocks is based on the maturity index proposed in (Nesbitt and Young, 1982), i.e., $\text{CIA} = 100[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}_{\text{sil}} + \text{Na}_2\text{O} + \text{K}_2\text{O})]$, which reflects the degree of plagioclase preservation in terrigenous rocks. The CIA value equals to 51–54 in the Chupa metasediment, 50 in feldspars, and 45–55 in granites. The wide range of CIA values (52–69) in the coarse-grained garnet–biotite gneiss with kyanite is an optional evidence of its secondary nature.

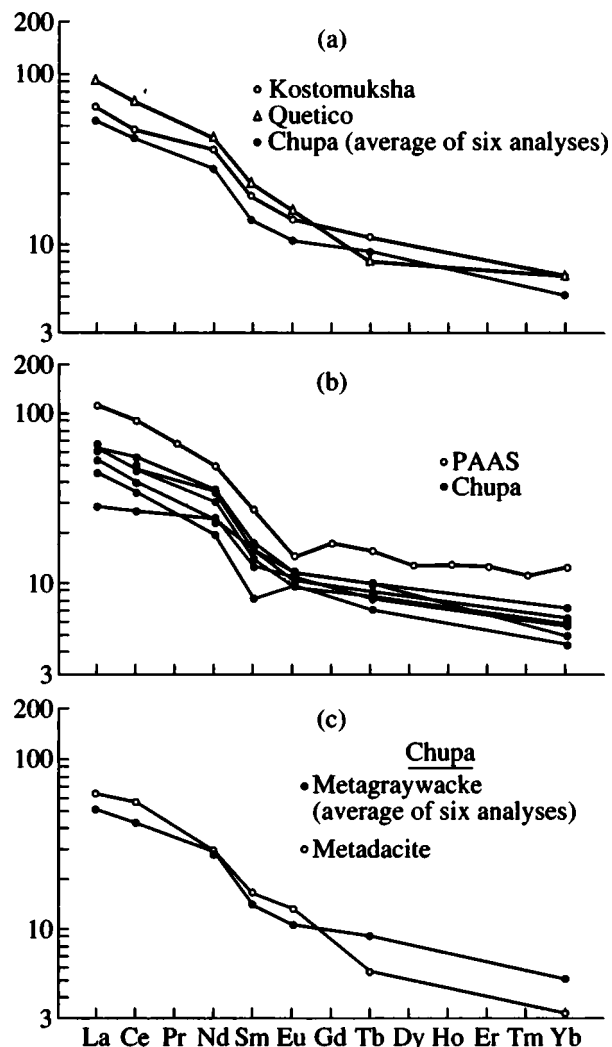


Fig. 10. The REE distribution in the Chupa Sequence metagraywacke, relative to: (a) Kostomuksha metasediment, Western Karelia (Mil'kevich and Myskova, 1998) and Quetico Subprovince, Canada (Sawyer, 1986), (b) PAAS (Nance and Taylor, 1976), and (c) Chupa Sequence metadacite.

Since the studied metasediments are immature and poorly sorted, their primary composition is significantly governed by the composition of source rocks. However, conglomerates are missing in the studied sequence, and we have only indirect information about the composition of source rocks. The geochemical data suggest a mixed source for the Chupa metagraywacke. The composition of studied rocks is only approximately similar to that of intermediate volcanic rocks. They are enriched in Na_2O and Sr owing to the influence of an acid source enriched in plagioclase. Simultaneously, they are enriched in MgO , FeO , TiO_2 , Cr, Ni, V, and Co, indicating a significant endowment of mafic and ultramafic components. Based on the Cr/Ti–Hf/Yb diagram (La Fleche and Camire, 1996), we estimated the approximate model composition of provenance

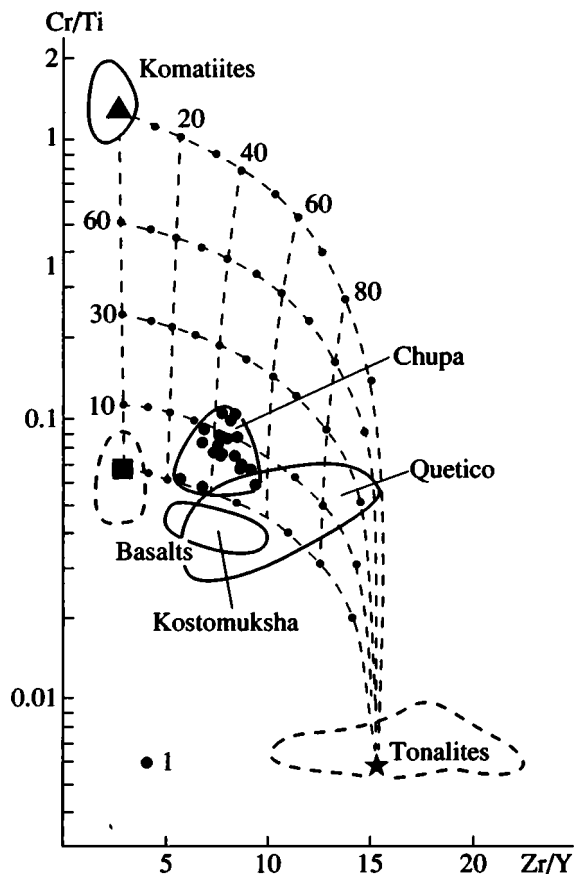


Fig. 11. The Cr/Ti–Zr/Y plot (Camire *et al.*, 1993) modeling the mixing of komatiites, basalts, and tonalites. (1) Chupa metagraywacke. Compare with domains of metasediments from Kostomuksha (western Karelia) and Quetico (Canada).

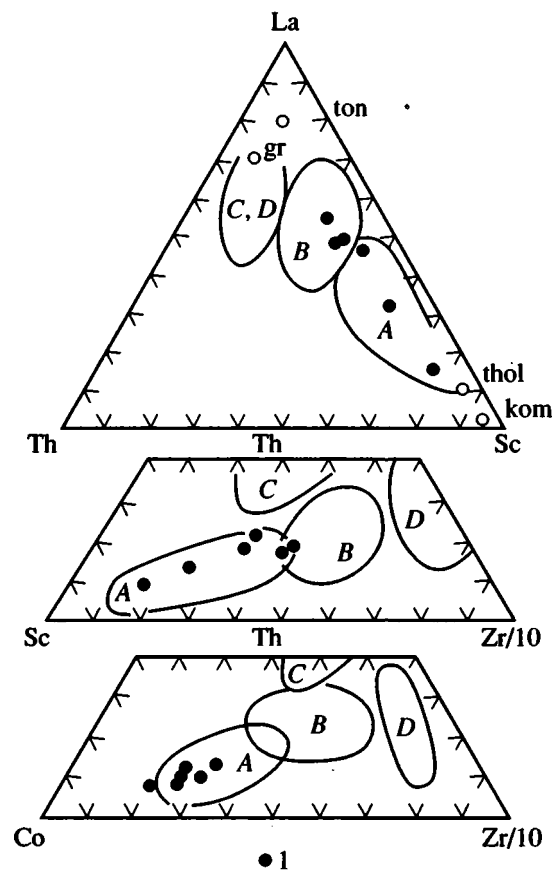


Fig. 12. Position of the Chupa metagraywacke in Bhatia's discriminant plots (Bhatia, 1983). (A) Oceanic island-arcs; (B) continental island-arcs; (C) active continental margins; (D) passive continental margins. (gr) Granite; (ton) tonalite; (kom) komatiite; (thol) tholeiite. (1) Chupa metagraywacke.

rocks (Fig. 9) and found that the Chupa metagraywacke could originate as a result of the washout of Archean rocks having as much as 70% tonalites (or dacites), 20% mafic components, and 10% ultramafic components.

In order to check the reliability of our conclusions, we compared metasediments in the Chupa Sequence with the Late Archean sequence in western Karelia and Canadian Shield where primary sedimentary structures are preserved. According to Pettijohn's classification (Pettijohn *et al.*, 1973), these rocks fall into the group of metagraywackes (Fig. 5). Based on major element contents, the Chupa paragneiss is akin to the Kostomuksha Formation metasilstone (Mil'kevich and Myskova, 1998) and the typical Archean graywacke (Taylor and McLennan, 1988), except for a slight enrichment in SiO_2 and CaO but depletion in K_2O and Al_2O_3 . Relative to the Quetico Superbelt metagraywacke (Sawyer, 1986), the Chupa paragneiss is enriched in SiO_2 and depleted in K_2O . The Chupa metagraywacke is also distinguished by higher concentrations of Cr and other iron group elements, along with

higher values of the Cr/V ratio, testifying to a significant endowment of the ultramafic component (table).

Metagraywackes from Chupa, Kostomuksha, and Quetico are similar in the REE distribution (Fig. 10a). Relative to the Phanerozoic PAAS, they lack the Eu anomaly and are more depleted in REE (Fig. 10b). Relative to the associated metadacite, the Chupa metagraywacke is characterized by a lesser slope of the REE distribution curve owing to an enrichment in HREE and depletion in LREE (Fig. 10c). The compositional variation of metagraywackes in the study region is likely to be induced by compositional differences of provenances (Fig. 11).

The enrichment of the Chupa metagraywacke in Cr and Ni, coupled with the availability of mafic and ultramafic components in the model source, suggests that the studied terrigenous rocks were possibly accumulated in a fore-arc basin. This conclusion can also be derived from Fig. 12 showing the La–Th–Sc, Th–Sc–Zr/10, and Th–Co–Zr/10 discriminant diagrams (Bhatia, 1983), where datapoints of the Chupa

metasediment fall into the domain of oceanic (and partly continental) island-arcs.

The analysis of major plutonic and supracrustal rocks, as well as structural and geochronological data, are needed for a more confident conclusion.

CONCLUSION

In the studied Chupa stratotype section, only the unaltered, fine-grained garnet–biotite gneiss, which is preserved as subordinate and thin relic bodies, can be referred to as the primary gneiss. The migmatized, coarse-grained, kyanite-bearing garnet–biotite gneiss, which prevails in the section, is most likely to be a restitic variety formed during the migmatization of the fine-grained gneiss.

Most fine-grained gneisses are represented by weakly differentiated metagraywackes varying in composition from sandstones to siltstones. The low CIA value (51–54), coupled with the positive correlation of K_2O and Al_2O_3 with MgO , are indicators of a low degree of chemical weathering, low maturity of provenances, and insignificant transportation of the terrigenous material. The mixed source is presumably composed of 70% tonalites (or dacites), 20% mafic rocks, and 10% ultramafic rocks. Dacites are only represented by a minor group of fine-grained gneisses.

With respect to the major element and REE distribution, the Chupa metasediments are similar to rocks of the graywacke–argillite series from some Late Archean greenstone belts, particularly Kostomuksha (western Karelia) and Quetico (Canada), except for elevated Cr concentrations and the model composition of provenance rocks. These features testify to differences in sedimentation conditions and rule out the possibility to reconstruct the geodynamic setting by a simple analogy model. In addition to geochemical data, a more diverse and comprehensive information is needed for the resolution of this problem.

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SHORT COMMUNICATIONS

Iron and Manganese Minerals in Suspended Matter from the Barents Sea

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Abstract—The mineralogy of suspended matter from surface and bottom waters is studied at two sites in the Barents Sea. Along with terrigenous minerals, the suspended matter samples contain authigenic mineral phases of iron and manganese oxyhydroxides. Mn-feroxyhite, Fe-vernadite, goethite, and proto-ferrihydrite were identified in samples from surface waters, whereas birnessite and nonferruginous vernadite were registered in samples from bottom waters. The formation of suspended manganese minerals in bottom waters is explained by an additional Mn supply from underlying reduced sediments during their early diagenesis and oxygen depletion in the near-bottom nepheloid layer. Bacteria are supposed to take part in the authigenic mineral formation.

The marine suspended matter includes various forms of Fe and Mn as components in terrigenous minerals, biogenic remains, organic matter particles, clay minerals, carbonate foraminiferal tests, and terrigenous (or authigenic) free oxyhydroxides. Manganese oxyhydroxides also occur as films on bacterial cells within “sea snow” flakes collected by sediment traps. However, mineral phases of authigenic iron and manganese oxyhydroxides are poorly studied up to date, and nothing is known about their mineralogy in the suspended matter from Arctic seas. This work is a first attempt to fill in the gap in our knowledge.

MATERIALS AND METHODS

We present the results of mineralogical and geochemical studies of suspended matter samples from two sites (Fig. 1, Table 1), namely the Central Barents Sea (Station 847, Cruise 11 of the R/V *Akademik Sergei Vavilov*, 1997) and the eastern nearshore area of the Pechora Sea (Cruise 13 of the R/V *Akademik Sergei Vavilov*, 1998).

Water column samples for the suspended matter extraction were collected using a 30-l plastic water bottle, and surface water samples were taken by a pail. The water samples obtained (from 1 to 10 l) were filtered through nuclear filters, 17 mm in diameter, with pores 0.45 μm , which were weighed beforehand. Filters were dried at 50°C and repeatedly weighed to determine the suspended matter concentration in water.

Vertical curves of light attenuation coefficient were measured at all stations of the R/V *Akademik Sergei Vavilov* (cruises 11 and 13). Using the empirical equation by (Aibulatov *et al.*, 1999), we calculated the suspended matter concentration from the coefficient values.

Specimens for the mineralogical study were prepared applying the suspension technique with a UZDN-A ultrasound dispersator. Specimens were studied using a JEM-100C electron microscope equipped with goniometer (inclination angle $\pm 60^\circ$) and with a KEVEX-5100 energy-dispersive device. Electron microscope images, energy-dispersive spectra, and electron diffraction patterns were obtained for each particle studied.

The bulk chemical composition of suspended matter was determined using a VRA-30 X-ray fluorescence device in the Analytical laboratory, Institute of Oceanology, Russian Academy of Sciences (analyst T.G. Kuz'mina).

RESULTS

The suspended matter concentration in the near-bottom nepheloid layer at Station 847, located on the southern slope of the Central Barents Sea rise, ranges within 0.4–0.6 mg/l (based on light attenuation measurements). It rapidly decreases upward to values less than 0.2 mg/l that are typical of the transparent intermediate water layer. The well-developed surface nepheloid layer (0–30 m) has a suspended matter concentration of 0.4–0.6 mg/l (Aibulatov *et al.*, 1999).

Based on the mineralogical analysis of suspended matter, samples from surface (0 m) and near-bottom nepheloid layers contain the following terrigenous minerals (sum of minerals determined in a filter is 100%): quartz (25–28%), feldspars (15–18%), chlorite + kaolinite (15–44%), illite (20–22%), and poorly crystallized mica aggregates (5%). Among iron and manganese oxyhydroxides, the surface sample contains Mn-feroxyhite and a minor amount of Fe-vernadite. The Mn-feroxyhite is absent in the near-bottom suspended

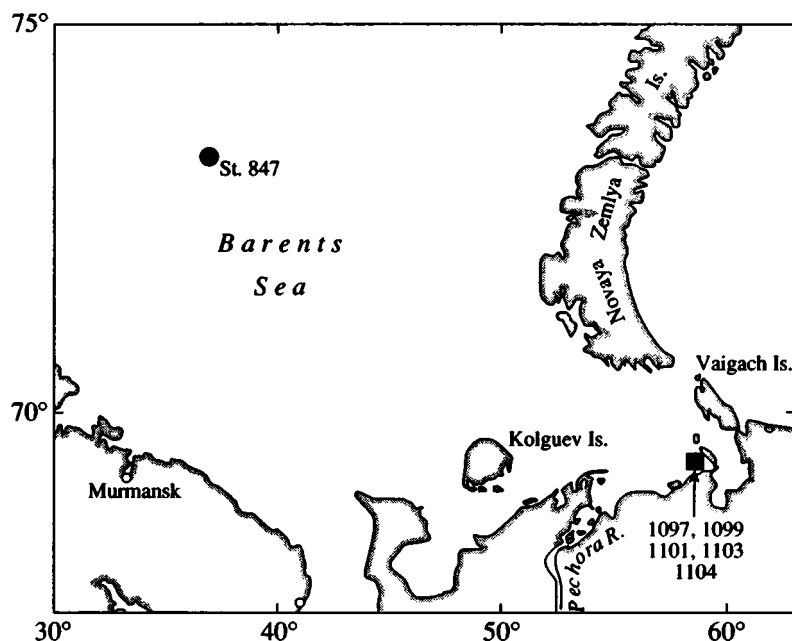


Fig. 1. Location of suspended matter sampling stations.

matter sample, and only manganese minerals (vernadite and rare birnessite flakes) occur here. The nonferrous vernadite is similar to hexagonal birnessite in morphology and composition (Figs. 2b, 2c). However, electron diffraction patterns of this mineral show only basal reflections $hk0$ (Gorshkov *et al.*, 1997).

In the eastern Pechora Sea, suspended matter samples were studied from the surface water of closely located stations 1099, 1101, 1103, and 1104, as well as from water column (0–15 m) at Station 1097. The terrigenous material is represented by the same minerals as at Station 847, but relationships between the minerals are highly variable: quartz from 5–6 to 43–45%, feldspars from 10–13 to 36%, chlorite + kaolinite from 23–26 to 30–36%, illite and mica (mainly mica aggregates) about 10%.

Among iron and manganese oxyhydroxides, Mn-feroxyhite predominates in surface samples, and minor amounts of proto-ferrihydrite were determined at sta-

tions 1101 and 1104 (Fig. 2a). Electron diffraction patterns of proto-ferrihydrite show two relatively wide ring reflections with d values 2.5 and 1.5 Å, indicating such an ultradispersivity of this phase that only the two-dimensional structural periodicity of the mineral is preserved. Proto-ferrihydrite particles have a bacteria-like habit. The habit and crystallinity are an evidence of authigenic origin of the mineral.

Goethite is observed in suspended matter samples from subsurface water layers (1, 3, 7, 11, and 15 m) at Station 1097, while the nonferruginous vernadite occurs in near-bottom samples (11 and 15 m).

The chemical composition (Table 2) characterizes the terrigenous (aluminosilicate) constituent of the suspended matter, whereas the contribution of authigenic oxyhydroxides of iron and especially manganese, is practically negligible. The extremely low content of suspended Mn even in nearshore waters confirms the idea about Mn migration mainly in dissolved forms.

Table 1. Data on sampling stations

ASV station numbers	Coordinates		Water depth, m	Sampling depth, m
	N	E		
847	73°25'	37°00'	234	0.230
1097	69°07'	58°17'	17	0, 1, 3, 7, 11, 15
1099	69°06'	58°02'	20	0
1101	69°01'	58°20'	15	0
1103	69°05'	58°39'	15	0
1104	69°10'	58°21'	18	0

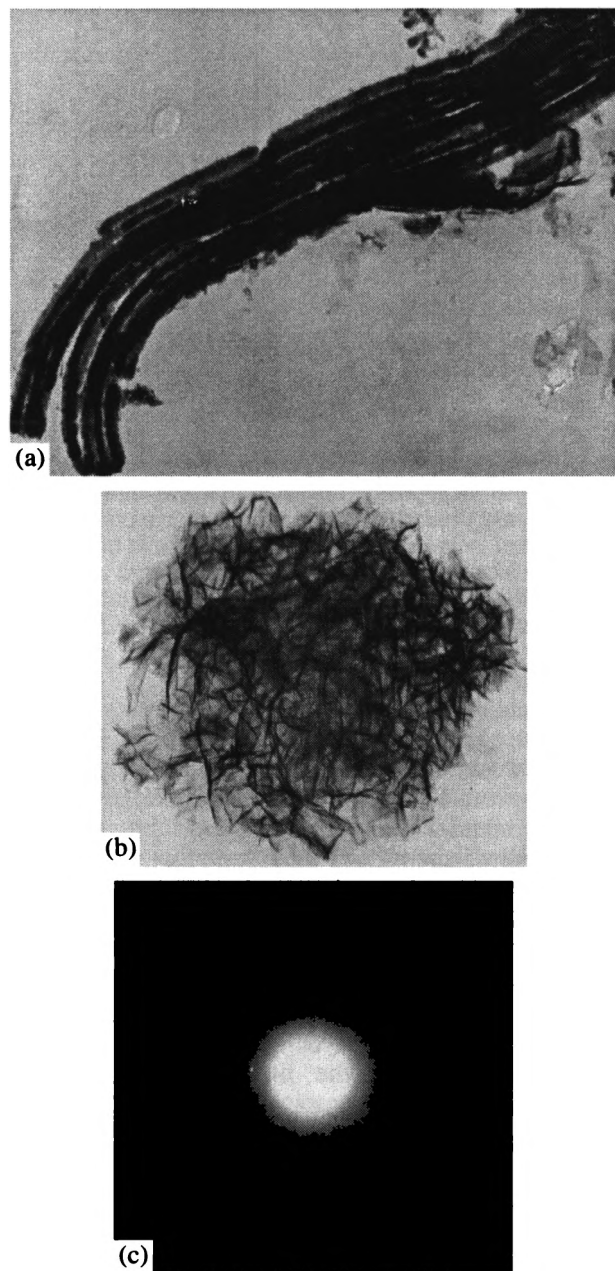


Fig. 2. SEM images of (a) the bacteria-like particle of proto-ferrihydrite, magn. 30000 and (b) nonferruginous vernadite, magn. 35000; (c) electron diffraction pattern of nonferruginous vernadite.

The concentration of suspended Fe and Fe/Al ratio values vary within the limits common for the terrigenous particulate material.

DISCUSSION

The mineralogical study revealed a presence of crystalline mineral phases of iron and manganese oxyhydroxides in the suspended matter of both surface and

bottom waters from the central Barents Sea and near-shore area of the Pechora Sea.

The Mn-feroxyhite is pervasive in the suspended matter of surface layer from both regions. Vernadite is also found at Station 847, while proto-ferrihydrite occurs at stations 1067–1104. In the near-bottom nepheloid layer, both Mn-feroxyhite and proto-ferrihydrite are absent. If we exclude the probably terrigenous goethite registered in the suspended matter from subsurface waters (1–11 m) at Station 1097, only manganese minerals (vernadite and rare birnessite flakes) occur in the near-bottom nepheloid layer.

The separation of iron and manganese minerals between surface and near-bottom nepheloid layers seems to be regular. It possibly reflects different physicochemical environments (oxic regime, Eh, pH, and concentration of dissolved Fe and Mn) of the authigenic mineral formation. We have also to consider the role of biogeochemical processes and bacterial activity. One of possible explanations is presented here as a preliminary hypothesis.

The near-bottom nepheloid layer is underlain in both study sites by Holocene organic-rich sediments, where an intense (early diagenetic) sulfate reduction develops to form hydrotroilite. In a strongly reduced environment within the sediments, Mn is turned into the soluble bivalent form, and diffuses to the bottom water. The bioturbation and repeated suspension of the surface sediment layer promotes the enrichment of the bottom water in dissolved Mn.

The reactive Fe^{2+} is bound in hydrotroilite and pyrite during the sulfate reduction. A part of the dissolved Fe^{2+} migrates from the reduced zone to the sediment surface. The Fe^{2+} is oxidized at the redox barrier, enriches the surface layer of sediments, and forms ferruginous nodules. Platy and biomorphic tubular nodules, which occur at the redox boundary within sediments at Station 847, contain hematite and common feroxyhite. As it was shown by Drits *et al.* (1995), hematite can be formed during the transformation of metastable ferrihydrite that contains ultradispersive hematite. Proto-ferrihydrite was not found in the suspended matter at Station 847, but it was registered in the suspended matter from surface water of the Pechora Sea.

The oxygen consumption for the organic matter decay leads to its depletion in the bottom water. The abundance of organic matter as suspension in the bottom water and sediment on the bottom creates a favorable environment for bacterial activity.

The crucial role of bacterial activity in creating favorable physicochemical conditions for birnessite precipitation was previously shown in several publications (Dubinina, 1978; Gorshkov *et al.*, 1992). Nonferruginous vernadite flakes associated with birnessite flakes represent products of the bacterial replacement of birnessite.

The combination of conditions listed above possibly leads to relative enrichment of the near-bottom nepheloid layer in dissolved Mn and separation of Mn from reactive Fe that is conserved in sediments and nodules. We believe that this process creates prerequisites for the precipitation of pure manganese minerals (nonferruginous vernadite and in some cases birnessite) on the suspended matter particles. Manganese minerals in the near-bottom suspended matter represent a link of Mn recycling, and they do not directly participate in the formation of sediments or nodules dominated by iron phases.

In the surface nepheloid layer, which is isolated from the near-bottom one by the transparent intermediate water, the additional Mn flux from sediments is absent. Oxyhydroxide minerals of Fe and Mn precipitate here on suspended matter particles under conditions of background Fe and Mn concentrations in seawater and oxygen saturation. The surface layer mainly contains ferruginous minerals, such as Mn-feroxyhite, and in some cases proto-ferrihydrite, whereas manganese phases are rare.

Particles of proto-ferrihydrite reveal a distinct bacterial morphology. This is an evidence for bacterial origin of the mineral. A similar iron hydroxide representing the bacterial structure (*Gallionella*), which contains opaline silica, was identified earlier in some hydrothermal deposits (Gorshkov *et al.*, 1989, 1992a, 1992b). The ultradispersive proto-ferrihydrite phase was likely formed as a result of rapid biogenic precipitation. The presence of silica serves as an additional factor leading to low crystallinity of the mineral phase described.

CONCLUSION

(1) Authigenic crystalline phases of iron and manganese oxyhydroxides are identified in the suspended matter from both the central Barents Sea and the near-shore area of the Pechora Sea. Mainly ferruginous minerals (Mn-feroxyhite and proto-ferrihydrite) occur in the surface water, whereas Fe-vernadite is rare here. Manganese minerals (nonferruginous vernadite and rare birnessite) are fixed in bottom waters.

(2) We suggest that the separation of iron and manganese phases results from an additional input of dis-

solved Mn from sediments into the bottom water during the reductive diagenesis. Oxygen deficiency in the near-bottom nepheloid layer promotes this process.

(3) The precipitation of iron and manganese minerals in the suspended matter is related to bacterial activity. It represents a side effect of iron and manganese cycles in the sea, and these minerals are not directly participating in the sediment or nodule formation.

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CHRONICLE

The 75th Birthday of Vladimir Nikolaevich Kholodov



Vladimir Nikolaevich Kholodov, Chief Editor of the Journal *Lithology and Mineral Resources*, DSc (Geol.-Miner.), Professor, Academician of the Russian Academy of Natural Sciences (RANS), the USSR State Prize laureate, Chief Researcher of the Geological Institute, Russian Academy of Sciences (RAS), turned 75 years of age on August 21, 2000.

Kholodov belongs to a generation of scientists, whose conscious life began during the Great Patriotic War. After finishing high school in 1943, he joined the Army and participated in military operations of the First Ukrainian Front and the Leningrad Front for two years, first as a radio telegrapher and later as head of a radio station. For his activity in the labour front and in the Army, Kholodov was awarded the Medal for the Defence of Moscow, the Medal for the Victory over Germany, the Order of the Patriotic War (II Class), and 11 anniversary medals.

Upon termination of the war and demobilization, Kholodov entered the Geological Prospecting Faculty of the Gubkin Oil Institute in Moscow, which he grad-

uated from in 1951. His scientific interests were focused at that time on studying uranium deposits in Paleogene carbonate rocks of the Fergana Valley.

Under the supervision of Prof. L.V. Pustovalov, V.I. Danchev, and T.A. Lapinskaya, Kholodov carried out prospecting for uranium deposits in the Expedition 1 of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM). He pointed out a multistage formation of deposits of uranium and other elements in carbonate rocks, revealed the controlling role of epigenetic processes in the formation of these ore deposits, suggested a new concept of ore genesis, and unravelled the role of groundwater in the formation of ores and transformation of carbonate rocks. Using the Shakhtar deposit as an example, Kholodov and his colleagues substantiated the concept of the epigenetic mineralogical and geochemical zonation. This concept was later used as the basis for prospecting and exploration of exogenic and epigenetic uranium deposits.

In 1955, Kholodov got his PhD degree. In 1957, he was invited by K.A. Vlasov, Corresponding Member of the USSR Academy of Sciences, to join the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements (IMGRE), where he headed a team of lithologists and geochemists to study formation conditions and distribution features of sedimentary and volcanosedimentary deposits of rare elements.

The work resulted in the systematization of a great deal of documentary material on different types of rare element deposits in sedimentary rocks, the elaboration of new principles of their classification, and the compilation of various genetic schemes, which explained the generation of facies, formational, and other types of rare metal deposits in sedimentary strata.

The results obtained by researchers from the IMGRE were published in a three-volume monograph *Geochemistry, Mineralogy, and Genetic Types of Rare Element Deposits* (Moscow: Nauka, 1966). In 1967, Kholodov and other key researchers of the IMGRE was awarded the USSR State Prize for this work, which was of great theoretical and economic importance. The monograph was translated into English.

In December, 1965, Kholodov became a senior researcher of the Sector of Volcanosedimentary Formations at the Geological Institute of the Academy of Sciences. He scrutinized stratiform lead–zinc deposits in Devonian carbonate rocks of Central Asia, as well as lithofacies conditions of the formation of pelletal phosphorite strata in Cambrian rocks of the Karatau Range

(Kazakhstan). In a series of publications, Kholodov demonstrated that vanadium-bearing black shales and phthanites formed in a relatively deep sector of the Cambrian paleobasin, whereas phosphorite strata accumulated in littoral areas near the coast of a strait-shaped sea basin.

In 1970, Kholodov successfully defended the DSc dissertation *Sedimentary Vanadium Concentrations, Their Types, Distribution Regularities, and Genesis*, in which he discussed ways of the migration and concentration of vanadium in the hypergene zone, classified deposits of vanadium ore and associated minerals, and described various mechanisms of vanadium ore formation. Kholodov also showed that large vanadium resources are related to the oldest magmatic deposits. Various sedimentary vanadium deposits are usually associated with younger sedimentary sequences, and in most cases formed due to hypergene redeposition of magmatic accumulations. The voluminous material collected during this period provided the basis for the book *Sedimentary Ore Genesis and Vanadium Metallogeny*, which was awarded the prize of the Moscow Society of Naturalists (MOIP).

In 1970, Kholodov started work under the supervision of Academician N.M. Strakhov. In 1975, he was nominated Head of the Laboratory of Geochemistry of Sedimentary Rocks in the Geological Institute.

For many years, Kholodov and his colleagues studied the alternating lithofacies, geochemical, and paleogeographic conditions in the Crimean and Caucasus regions during the Mesozoic and Cenozoic. The comparative lithogeochemical studies of Miocene deposits in the Caucasus, as well as recent sediments in the Black and Caspian seas made it possible to decipher lithofacies, geochemical, and paleogeographic conditions of the formation of black shales, quartz sandstones, and marls. They also promoted the reconstruction of mineralogical and geochemical features of diagenesis, catagenesis, and metagenesis in old sedimentary rocks. Regularities in the distribution of chemical elements in Middle Miocene oil-hosting deposits were characterized on the basis of the absolute mass method. The data were presented in the book *Lithology and Geochemistry of Middle Miocene Rocks from Eastern Cis-Caucasia* written in collaboration with R.I. Nedumov.

In subsequent works, Kholodov developed these ideas and showed the role of clay mineral transformation (illitization of montmorillonite) in the selfpurification of clays from bitumoids, carbon dioxide, hydrogen sulfide, and silica. He also considered genetic schemes of the formation of clastic dikes and other traces of sandy diapirism. He suggested a new hypothesis of the origin of anomalously high stratal pressure, mud volcanoes, and oil-and-gas fields. Finally, Kholodov substantiated the general theory of catagenetic transformations of sedimentary rocks. He proposed to distinguish the infiltrational, elisional, and gravitational-brine pro-

cesses. He also described different types of geochemical-mineralogical zonation and ore deposit related to the realization of the above-mentioned phenomena. The theory of catagenetic processes well accounts for the genesis of hydrothermal ore-bearing solutions, stratiform deposits, and oil-and-gas accumulations without relating it to magmatic processes. Kholodov presented all these ideas in his book *Postsedimentation Transformations in Elisional Basins*, and the practical application of the ideas in the book *Massive Sulfide Deposits of the Greater Caucasus* written in collaboration with Z.R. Kiknadze.

Kholodov developed ideas of the vanadium geochemistry and suggested a theory of the provenance evolution in the Earth's history. The successive replacement of the oldest basalts, basic effusives, granitoids, gabbro-anorthosites, and sedimentary rocks in the continental provenance was essentially reflected on the geochemistry of almost synchronous sediments.

The evolution of provenances in continental blocks well explains the origin of iron ore and manganese ore belts on the Earth and many other traces of irreversible development of geological processes.

In collaboration with Corresponding Member of the RAS P.P. Timofeev, Kholodov elaborated a hypothesis of the evolution of sedimentation basins in the Earth's history. Based on the analysis of the relief history, the hydrogeological analysis of free hydrosphere, as well as the examination of environmental constraints of the sedimentary cover of the World Ocean, they showed that sedimentation basins evolved in the following succession: lakes and lake-type water bodies—intracontinental and marginal seas—oceans. Oceans probably appeared at the Mesozoic–Cenozoic stage of the Earth's history and were absent in the Paleozoic and Precambrian.

In recent years, V.N. Kholodov and R.K. Paul revised ideas of the chemogenic origin of pelletal phosphorite strata related to upwelling (the hypothesis elaborated by A.V. Kazakov and G.N. Baturin). On the basis of several facts, the authors came to the conclusion that the influx of P_2O_5 from continents into Cambrian seas was a terrigenous process. Its dissolution and concentration occurred under conditions of hydrogen sulfide contamination of bottom water in the stagnation regime. Finally, it precipitated on shoals came about by the biogenic–chemogenic process with a direct participation of cyanobacteria and algae.

Kholodov has more than 310 publications, including 8 monographs. One monograph and 42 papers in scientific journals were translated into English. He is a Member of the International Association of Sedimentologists (IAS). Kholodov is actively engaged in scientific organizational works. Since 1967, he has been working in the Editorial Board of the Journal *Lithology and Mineral Resources*, first as Executive Secretary and Deputy Editor-in-Chief and, since 1980, as Editor-in-Chief. The journal has a good scientific reputation in

Russia and abroad. It is translated into English since 1967.

As the First Vice Chairman of the Interdepartmental Lithological Committee (ILC), Kholodov took an active part in the organization of the 27th Session of the International Geological Congress, four All-Union lithologic conferences, and a series of plenary sessions. Taking charge of the Section of the Lithology of Rare and Base Metal Ores of the ILC, he organized and hold four All-Union seminars. He was the editor of 30 collections of articles and monographs published by the Mir, Nedra, and Nauka Publishing houses.

He has been reading a Specialized Course devoted to Geochemistry of the Sedimentary Process for the last 10 years at the Department of Lithology and Marine Geology of the Geological Faculty, Moscow State University (MGU). A relevant textbook is under preparation for publication. In March 1991, Kholodov was elected Member of the Russian Academy of Natural Sciences (RANS) where he took charge of the Scientific Council on Problems of Geochemistry and Cosmochemistry.

Kholodov is working hard as the Chairman of the Commission on the Scientific Heritage of Academician N.M. Strakhov, as well as a member of the Editorial Board of the Journal *Geology of Ore Deposits* and three specialized councils on DSc dissertations at the Geological Institute, Gubkin State Oil and Gas Academy, and Moscow State University.

Vladimir Nikolaevich Kholodov meets his 75th birthday in the prime of his creative life. He is endowed with enthusiasm and devotion to science, great capacity for work, inexhaustible energy, strong adherence to scientific principles, and high creative potential.

His friends and colleagues warmly congratulate him and wish much success, health, and joy!

*Editorial Board of the Journal
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Lithologists of the Geological Institute,
Russian Academy of Sciences*

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